

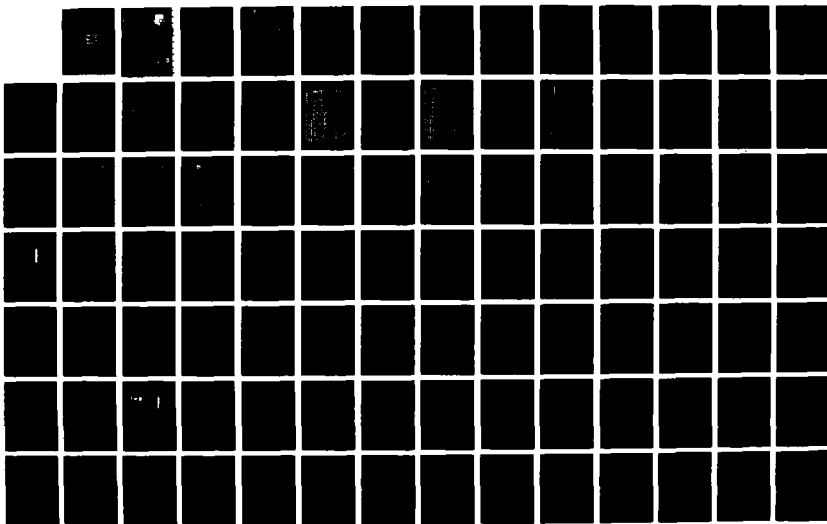
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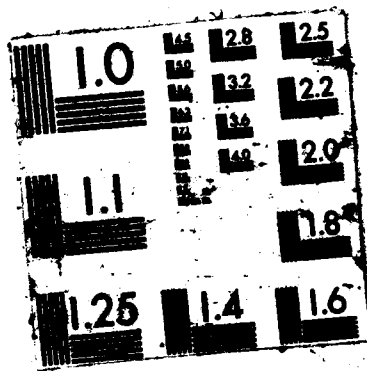
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Part II

AVIATION TURBINE FUELS FROM TAR SANDS  
BITUMEN AND HEAVY OILS

Part II Laboratory Sample Production

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JULY 1, 1987

Interim Report for Period 1 April 1984 - 31 May 1985

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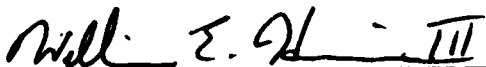
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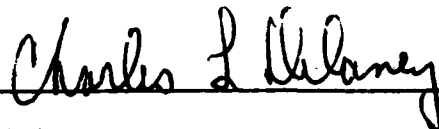
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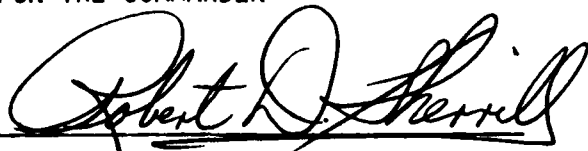


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Phase II work performed on small bench scale laboratory units was to validate the process variables identified in Phase I. As a part of this effort, samples (quantity 500 ML to 1000 ML) of JP-4 (MIL-T-5624L), JP-8 (MIL-T-83133A), were produced and submitted to AFWAL for their evaluation. Detailed characterizations of the tar sand feedstocks and product samples were performed. From the data generated in Phase II, specific goals and tests were outlined for Phase III of the program. <i>Keywords</i>		

## FOREWARD

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We are indebted to our Ashland colleague Mr. Robert E. Stone for his valued assistance in updating the process computer model based on data from Part II.

We also recognize the valued assistance of Ms. Sherry M. Connor and Ms. Lois Davis in the preparation of this report.

This report is Part II of three parts.



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## SECTION I

### INTRODUCTION

During the past two decades, energy resources have been critical to world and United States economic development and well-being. The world has moved from adequate supplies during the sixties, to thoughts of rationing in the early 70's, through adequate though tight supplies in the middle 70's, to limited supply and gasoline lines in the late 1970's, to overcapacity during the early 1980's. These swings in the supply/demand relationship have been particularly damaging to the United States, due to a high level of imported oil and volatile oil price structures.

Developing secure domestic energy resources is, and should be, a high priority for domestic security reasons. Federal programs to develop coal and oil shale resources are well known; noteworthy within this framework are earlier studies funded under Department of Defense (DOD) auspices.<sup>1-7</sup>

Another major resource available is tar sands bitumen and/or heavy oil. Attention has been brought to bear on this potential energy supply by DOD research contracts awarded to Suntech and Ashland Oil for evaluation of refining methods applied to these resources.

The objectives of these programs are to determine the cost, yield, chemical properties, and physical characteristics of variable quality aviation turbine fuels produced from tar

sand bitumen and heavy oil crudes. Ashland's program is designed to meet these objectives by adapting RCCSM process technology and other process technologies as necessary to produce optimum product slates.

This program keys on six major goals:

- Optimize the processing scheme
- Produce sample quantities of JP-4 and JP-8
- Achieve at least 70% energy efficiency
- Limit net coke and residual products to less than 10%
- Develop an economic model of the process
- Determine the economic effect of varying fuel quality

These goals are to be addressed in three major phases of activities:

Phase I. Preliminary Process Analysis

Phase II. Laboratory Sample Production

Phase III. Pilot Plant Testing, Final Design and Analysis

Phase I efforts were performed from July 1983 through March 1984. The Phase I study defined a significant potential heavy oil and tar sands resource, delineated a combination process with unique advantages in processing these materials,

---

RCCSM Process - Service Mark of Ashland Oil, Inc., for technical assistance and consulting services in connection with processes for heavy oil cracking and related catalyst.

and projected preliminary economics for processing four potential feedstocks. These materials, valued at \$25/barrel, were not economic in 1983 markets. Threshold market values were determined and the basis for further work defined. This effort is described in an interim technical report.<sup>8</sup>

This report summarizes Phase II work performed from April 1984 through May 1985. The key elements in this study were (1) characterization of four heavy oil and tar sand feedstocks, (2) laboratory measurement of process response, (3) laboratory sample production, and (4) updating the earlier economic estimates. Portions of this work have been previously reported.<sup>9</sup>

## SECTION II. FEEDSTOCK CHARACTERIZATION

The feedstocks provided for evaluation were Hondo and San Ardo heavy oils, both from California; Westken tar sand bitumen from West Central Kentucky; and Sunnyside tar sand bitumen from the Uinta Basin, Utah. Each of the feedstocks had unique characteristics: the Hondo was a high sulfur heavy oil, the San Ardo a medium sulfur, medium metals, medium carbon heavy oil, the Westken a high metals bitumen and the Sunnyside a high diluent low metals bitumen. The objective of this work was to provide a complete definition of the properties of the feedstocks under investigation. To accomplish this, each feedstock was fractionated into narrow-boiling cuts and each cut was analyzed in detail.

### Experimental Procedure

Drums of each oil were provided by the Air Force. A ten gallon sample of each of the four feedstocks was obtained from the drums. The Westken drum was placed in a steam cabinet for several hours before sampling. Each feedstock was mixed well before sampling, and the samples were withdrawn through a spigot on the drum top. About one gallon of the raw feedstock was evaluated for as-received properties and the remainder was charged to a 50-mm diameter x 300-mm length vacuum jacketed fractionation column with stainless steel helix packing.

The column was operated at 2:1 reflux ratio at atmospheric pressure to collect fractions in 100°F increments to 400°F, followed by vacuum to 800°F. The greater than 800°F residue was fractionated to a target atmospheric equivalent of 975°F on a modified Hempel apparatus at a vacuum of 1 mm Hg. Both weight and volume measurements were made on all fractions.

### Experimental Results

Physical and chemical properties and fractionation yields for each crude are shown in Tables 1-4. Table 5 is a summary comparison of the key analyses of the four full-range crudes, while Table 6 gives the properties of the residual components of each feed. Figures 1-9 portray these data graphically.

#### 1. Hondo

The Hondo Monterey heavy oil, Table 1, is found in the Santa Barbara Channel about three miles or more off-shore of California in the Santa Ynez deposit. Literature indicates that California heavy oils vary widely in properties but are typically low in asphaltenes with moderate sulfur and metals levels and high hydrogen content. The sample evaluated in Phase II, however, resembled a bitumen to some extent, as the asphaltene content (15.1%), the sulfur content (5%), and the metals level (>300 ppm nickel + vanadium) were all high. The low viscosity, high gravity and light components qualified the feedstock as a heavy oil rather than a bitumen.



TABLE 1

## TAR SAND/HEAVY OIL EVALUATION

SAMPLE TYPE: Hondo

SAMPLE NUMBER: 08-ND-70

ITEM / FRACTION	( ) 300	300- 400	400- 480	480- 580	580- 675	675- 765	765- 831	831- 972	972+	Feed
Yield, LV %	14.0	6.3	5.4	8.4	7.9	7.9	3.1	12.7	36.3	100
Yield, WT %	10.7	5.3	4.8	7.8	7.4	7.6	3.1	12.6	40.6	100
K Factor	12.2	11.6	11.52	11.48	11.55	11.50	11.58	11.55		11.6
API Gravity	65.8	44.6	38.2	32.0	28.2	22.9	21.0	16.5	1.9	18.0
Specific Gravity	.7172	.8035	.8334	.8654	.8860	.9164	.9277	.9560	1.0608	.9465
Carbon, WT %	-	-	-	-	-	-	-	853	79.4	81.06
Hydrogen, WT %	14.6	13.57	13.16	12.77	12.35	12.06	11.37	10.9	10.4	11.60
Nitrogen, ppm	2	30	133	610	900	0.27%	0.32%	0.33%	1.0%	0.34%
Basic Nitrogen, ppm	<1	21	0.01%	0.06%	0.10%	0.11%	0.12	0.12	-	-
Sulfur, WT %	.27	2.02	2.78	3.49	3.75	4.44	4.52	4.58	6.53	5.02
Oxygen, WT %	-	-	-	-	-	-	-	-	-	1.3%
Phenols, ppm	-	14	8	-	-	-	-	-	-	-
Iron, ppm	-	-	-	1	<1	<1	<1	1	21	8
Nickel, ppm	-	-	-	<1	<1	<1	<1	<1	176	70
Vanadium, ppm	-	-	-	<1	<1	<1	<1	<1	548	233
Sodium, ppm	-	-	-	<1	<1	2	7	19	403	89
Freeze Point, °F	-90-	-90-	-54-	-11.2	-	-	-	-	-	-
Ramsbottom Carbon	-	-	-	-	-	0.11	0.12	1.14	20.85	8.7
Saturates, Vol %	93.0	79.6	65.3	55.9	65.3	51.8	44.0	30.8	4.7	21.5
Olefins, Vol %	0.8	0.9	1.8	6.9	-	-	-	-	-	-
Aromatics, Vol %	6.2	19.5	32.9	37.2	34.7	48.2	56.0	48.5	24.6	24.5
Pour Point, °F	-	-	-	-	+42.8	+70	+30	-	-	-5
Viscosity, 100°F, CS	0.5	1.03	1.73	3.19	7.19	-	-	-	-	-
Viscosity, 140°F, CS	-	-	-	-	-	9.60	19.67	-	-	-
Viscosity, 210°F, CS	-	-	-	-	-	3.74	6.14	13.67	-	20.6
Viscosity, 275°F, CS	6.9	55	-	-	-	-	-	-	17.34	-
RON	3	1	-	-	-	-	-	-	-	-
RVP	-	-	-	-	-	-	-	-	-	-

\*By Gel HPLC

Volumetric yields showed a surprising 25% boiling below about 500°F making this the lightest of the four feedstocks evaluated. Fractionation could yield 25% or more virgin turbine fuel. This fraction would require hydrotreatment to remove sulfur and nitrogen.

K factor and API gravities for this feedstock were generally higher than the comparable fraction of the other three crudes. Hydrogen content, as expected, was also higher. The lower boiling components contain hydrogen levels approaching that necessary for turbine fuel. Sulfur is high throughout the boiling range and nitrogen is also high, especially in the higher boiling fraction.

Metals and asphaltenes were concentrated in the highest boiling fraction. Of significance was the salt content of this crude (90 ppm). Normally, crude desalting would be necessary before cracking since sodium is a catalyst poison. Conventional desalting processes could be used. However, in the metals removal step (ART<sup>SM</sup>), which is recommended for this feed, sodium is removed with the metals on an adsorbent. The final treatment scheme will be determined by economics.

---

ART<sup>SM</sup> is a service mark of Engelhard Corporation for professional services relative to selective vaporization processes for removing contaminants from petroleum feedstocks.

## 2. Westken Tar Sands Bitumen

The Westken bitumen, Table 2, comes from a deposit located in Edmonson County, Kentucky, near the southeastern rim of the Illinois basin. Our characterization of the bitumen confirmed published analyses. The Westken bitumen was heavy, with a 10.4° API gravity; the metals content was high at 300 ppm Ni + V, which is much higher than conventional reduced crude. The high pour point (65°F) and residuum content (>50%) indicated potential handling problems associated in distribution and processing of this material.

Sodium content was over 540 ppm, which was unexpected. With the low API gravity, desalting would be complicated by phase separation difficulties. A diluent would have to be used during this processing step and in the demetallization to facilitate handling and promote phase separation. Due to the diluent volumes required, larger equipment would be needed than had been projected in Phase I. A desalting step was not included in the Phase I model.

Volumetric yields showed virtually no virgin turbine fuel and about 50 volume percent heavy gas oil (600-1000°F). The Westken bitumen was overall the heaviest of the four feedstocks evaluated. K factors and hydrogen content were relatively high compared with the Sunnyside and San Ardo, but low compared with conventional petroleum feedstocks. Products from cracking were anticipated to be aromatic in

TABLE 2

# TAR SAND/HEAVY OIL EVALUATION

SAMPLE TYPE: Westken

SAMPLE NUMBER: 08-ND-30

ITEM / FRACTION	-300	500- 600	600- 660	660- 750	750- 841	841- 985	985+	Raw Feed
Yield, LV %	0.54	6.52	8.57	11.16	10.80	12.52	47.86	100
Yield, WI %	0.46	5.78	7.75	10.38	10.27	12.1	51.3	100
K Factor	11.77	11.38	11.42	11.42	11.44	11.5		11.2
API Gravity	34.1	28.6	25.4	21.1	17.8	15.3	0.90	10.4
Specific Gravity	0.8545	0.8838	0.9018	0.9273	0.9478	0.9639	1.0688	0.9972
Carbon, WI %	-	-	-	-	85.3	85.5	84.1	84.3
Hydrogen, WI %	13.17	12.89	12.55	12.02	11.58	10.7	10.8	10.9
Nitrogen, WI %	47ppm	55ppm	191ppm	758ppm	0.20	0.24	0.61	0.23
Basic Nitrogen, WI %	<10ppm	49ppm	133ppm	387ppm	0.16	0.10	-	-
Sulfur, WI %	0.30	0.55	0.95	1.32	1.44	1.32	1.94	1.66
Oxygen, WI %	-	-	-	-	-	-	-	1.93
Phenols, ppm	-	-	-	-	-	-	-	-
Iron, ppm	-	-	<1	<1	<1	<1	0.154	335
Nickel, ppm	-	-	<1	<1	<1	<1	114	63
Vanadium, ppm	-	-	<1	<1	<1	<1	458	229
Sodium, ppm	-	-	1	1	1	16	0.173	541
Ransbottom Carbon	-	-	-	-	-	0.50	15.29	11.02
Saturates, Vol %	75	65.1	31.8	12.8	16.5	*39.0	*11.1	*28.0
Olefins, Vol %	-	-	-	-	-	-	-	-
Aromatics, Vol %	25	34.9	68.2	87.2	83.5	42.5	16.7	24.1
Pour Point, °F	-	-10-	-10-	-10-	-5	-	-	65
Viscosity, 100°F, CS	-	-	-	-	-	-	-	-
Viscosity, 140°F, CS	1.54	2.90	5.05	14.59	36.93	-	-	-
Viscosity, 210°F, CS	-	1.54	2.31	4.07	8.76	26.12	-	186.27
Viscosity, 350°F, CS	-	-	-	-	-	-	1328	-
By Clay Gel HPLC	-	-	-	-	-	-	-	-

nature which would lead to naphthenic turbine fuels of relatively low API gravity.

Sulfur and nitrogen contents increased as the boiling range of the fractions increased. Both sulfur and nitrogen contents were moderate, with the sulfur content lower than that of the Hondo heavy oil. Asphaltene concentration in the residuum was 40 weight percent and about 20 weight percent in the total crude.

### 3. San Ardo Heavy Oil

The San Ardo field is located in the Coastal basin of the Salinas Valley, on-shore California. Literature indicates a moderate sulfur content and moderately high metals and residuum content. Ashland analyses showed sulfur at 1.8% and metals (Ni+V) at slightly over 140 ppm (Table 3). Ramsbottom carbon was 8.4% and asphaltenes 4.2%. With an API gravity of 14°, this crude had the possibility of being processed with little diluent.

With the exception of the high nitrogen content, the San Ardo crude has analyses which lie between those of the Hondo and Westken. Processability should therefore be a good compromise between these two, making it a desirable candidate for the Phase III work.

TABLE 3

# TAR SAND/HEAVY OIL EVALUATION

SAMPLE TYPE: San Ardo

SAMPLE NUMBER: 08-ND-128

ITEM / FRACTION	370	370- 430	430- 550	550- 640	640- 740	740- 846	846- 960	960+	Raw Feed
Yield, LV %	0.19	2.20	12.64	6.20	17.46	8.81	11.86	43.79	100
Yield, WI %	0.16	1.91	11.42	5.81	11.99	8.72	11.9	47.0	100
K Factor	11.29	11.36	11.28	11.18	11.20	11.32	11.33		11.39
API Gravity	40.4	36.2	29.6	23.8	19.8	15.5	13.6	4.1	14.0
Specific Gravity	0.8232	0.8437	0.8783	0.9111	0.9352	0.9626	0.9752	1.0438	0.9725
Carbon, WI %	-	-	-	-	-	-	86.1	84.3	84.80
Hydrogen, WI %	13.68	13.28	12.69	12.15	11.75	11.28	10.5	10.3	11.20
Nitrogen, WI %	19ppm	33ppm	180ppm	287ppm	0.16	0.36	0.45	1.34	0.91
Basic Nitrogen, WI %	16ppm	29ppm	212ppm	649ppm	0.11	0.16	0.22	-	0.24
Sulfur, WI %	0.48	0.35	0.56	0.86	1.08	1.44	1.43	2.49	1.83
Oxygen, WI %	-	-	-	-	-	-	-	-	0.89
Phenols, ppm	40	-	-	-	-	-	-	-	-
Iron, ppm	-	-	-	<1	1	1	<1	74	20
Nickel, ppm	-	-	-	<1	1	<1	<1	124	64
Vanadium, ppm	-	-	-	<1	<1	<1	<1	211	79
Sodium, ppm	-	-	-	4	1	1	12	37	5
Freeze Point, °F	-90-	-90-	-90-	-	-	-	-	-	-
Ramsbottom Carbon	-	-	-	-	0.10	0.10	0.40	19.90	8.43
Saturates, Vol %	-	86.0	76.0	65.1	36.7	34.4	33.7	36.4	30.8
Olefins, Vol %	-	-	-	-	-	-	-	-	-
Aromatics, Vol %	-	14.0	24.0	34.9	63.3	65.6	43.1	18.1	29.4
Pour Point, °F	-	-	-	-10-	-10-	0	-	-	25
Viscosity, 100°F, CS	-	1.51	2.82	7.90	-	-	-	-	-
Viscosity, 140°F, CS	-	1.10	1.86	4.33	10.4	55.86	-	-	-
Viscosity, 210°F, CS	-	-	-	-	3.76	10.76	35.83	-	72.38
Viscosity, 350°F, CS	-	-	-	-	-	-	-	308	-
*By Clay Gel HPLC									

#### 4. Sunnyside Tar Sands Bitumen

The fourth feedstock was the Sunnyside bitumen from the Uinta Basin, Utah. It was approximately 70% diluent (kerosene) and 25% resid (Table 4). Although this material was easy to handle, contained low metals and sulfur and had a high API gravity, physical and chemical properties varied from sample to sample. The diluent was not totally compatible with the bitumen as indicated by settling and precipitation in the drums received. A representative sample of the bitumen was impossible to obtain. A break in the K factor curve at about 550°F (Figure 2) shows the division between the diluent and the bitumen. Also, hydrogen content drops markedly at this point (Figure 3).

Metals and asphaltenes appear to be low, compared to expected levels, which emphasizes potential sampling problems. Phase I indications were that metals would total over 210 ppm. This sample should not be considered for Phase III work.

TABLE 4

# TAR SAND/HEAVY OIL EVALUATION

SAMPLE TYPE: Sunnyside

SAMPLE NUMBER: 08-ND-88

ITEM / FRACTION	-420	420 -470	470 -540	540 -665	665 -730	730 -805	805 -920	920+	diluent	feed
Yield, LV %	1.11	62.51	9.83	0.94	1.35	0.65	2.94	19.84	100	100
Yield, WT %	1.05	59.58	9.57	1.01	1.48	0.74	3.35	24.7	100	100
K Factor	11.91	11.92	12.0	11.20	11.37	11.06	11.37		11.99	11.8
API Gravity	45.9	44.0	41.2	23.1	20.5	15.4	14.6	2.1	44.0	34.9
Specific Gravity	0.7976	0.8063	0.8193	0.9153	0.9309	0.9632	0.9679	1.0588	0.8063	0.8504
Carbon, WT %	-	-	-	-	-	85.6	84.9	81.4	-	85.99
Hydrogen, WT %	14.17	14.02	13.80	12.48	11.81	10.6	10.4	10.7	13.94	13.69
Nitrogen, WT %	9ppm	7ppm	57ppm	636ppm	0.13	0.24	.19	0.27	16ppm	.08
Basic Nitrogen, WT %	5ppm	6ppm	39ppm	0.06	0.12	0.13	.13	-	16ppm	0.09
Sulfur, WT %	0.11	377ppm	0.10	0.35	0.33	0.36	0.23	0.37	498ppm	0.09
Oxygen, WT %	-	-	-	-	-	-	-	-	-	0.65
Phenols, ppm	<10	-	-	-	-	-	-	-	-	-
Iron, ppm	-	-	-	<1	<1	<1	<1	0.40%	-	34
Nickel, ppm	-	-	-	<1	<1	<1	<1	84	-	5
Vanadium, ppm	-	-	-	<1	<1	<1	<1	84	-	2
Sodium, ppm	-	-	-	2	2	1	21	461	-	6
Freeze Point, °F	-41.8	-31.0	-0.4-	-	-	-	-	-	-25.6	-
Ramsbottom Carbon	-	-	-	-	-	0.10	0.20	-	-	1.62
Saturates, Vol %	88.3	82.2	68.4	40.3	51.3	52.7	56.4	10.4	78.1	57.4
Olefins, Vol %	1.6	4.0	-	-	-	-	-	-	9.0	-
Aromatics, Vol %	10.1	13.8	31.6	59.7	48.7	47.3	28.9	15.6	12.9	31.8
Pour Point, °F	-	-	-	-10-	+5	+15	-	-	-	-10-
Viscosity, 100°F, CS	-	-	2.4	15.7	-	-	-	-	-	-
Viscosity, 140°F, CS	-	1.25	-	-	27.46	-	-	-	1.27	3.96
Viscosity, 210°F, CS	-	0.83	-	-	6.75	12.14	43.22	-	0.85	1.96
Viscosity, 450°F, CS	-	-	-	-	-	-	-	620	-	-
*By Clay Gel HPLC										



TABLE 5  
ANALYSES OF  
FULL RANGE CRUDES

	HONDO	WESTKEN	SAN ARDO	SUNNYSIDE <sup>1</sup>	SUNNYSIDE
GRAVITY, °API	18.0	10.4	14.0	34.9	14.3
ELEMENTAL ANALYSIS, WTZ					
HYDROGEN	11.6	11.0	11.2	13.7	
SULFUR	5.02	1.66	1.83	0.09	0.22
NITROGEN	0.34	0.23	0.91	0.08	0.27
OXYGEN	1.4	1.9	0.9	0.7	
MAJOR METALS, PPM					
NICKEL	70	63	64	5	12
VANADIUM	233	229	79	2	4
K FACTOR	11.6	11.3	11.3	12.0	11.5
RAMSBOTTOM CARBON, WTZ	8.8	11.0	8.4	1.6	(21.2) <sup>2</sup>
VISCOSITY, CS @ 210°F	20.7	186	72.4	2.0	44
POUR POINT, °F	-5	65	25	-10-	20
RESID, WTZ NORMALIZED	41	52	48	24	83
DILUENT, WTZ				70.2	

1 INCLUDES DILUENT

2 CONRADSON CARBON

TABLE 6

# RESIDUAL COMPONENT PROPERTIES

<u>CRUDE</u>	<u>WESTKEN</u>	<u>HONDO</u>	<u>SAN ARDO</u>	<u>SUNNYSIDE</u>
GRAVITY, °API	0.9	1.9	4.1	2.1
YIELD, WT%	52	41	48	24
ESTIMATED CUT, °F	985	972	960	920
ELEMENTAL, WT%				
HYDROGEN	10.8	10.4	10.3	10.7
NITROGEN	0.61	1.07	1.34	0.27
SULFUR	1.94	6.53	2.49	0.37
METALS, PPM				
IRON	1500	21	74	4000
NICKEL	114	176	211	84
VANADIUM	458	548	124	84
SODIUM	1700	403	37	461
RAMSBOTTOM CARBON	15.3	20.8	19.9	
COMPONENT TYPES				
SATURATES	11.1	4.7	6.4	10.4
AROMATICS	16.7	24.6	18.1	15.0
POLARS	30.7	35.3	46.6	28.3
ASPHALTENES	41.5	35.4	28.0	46.3

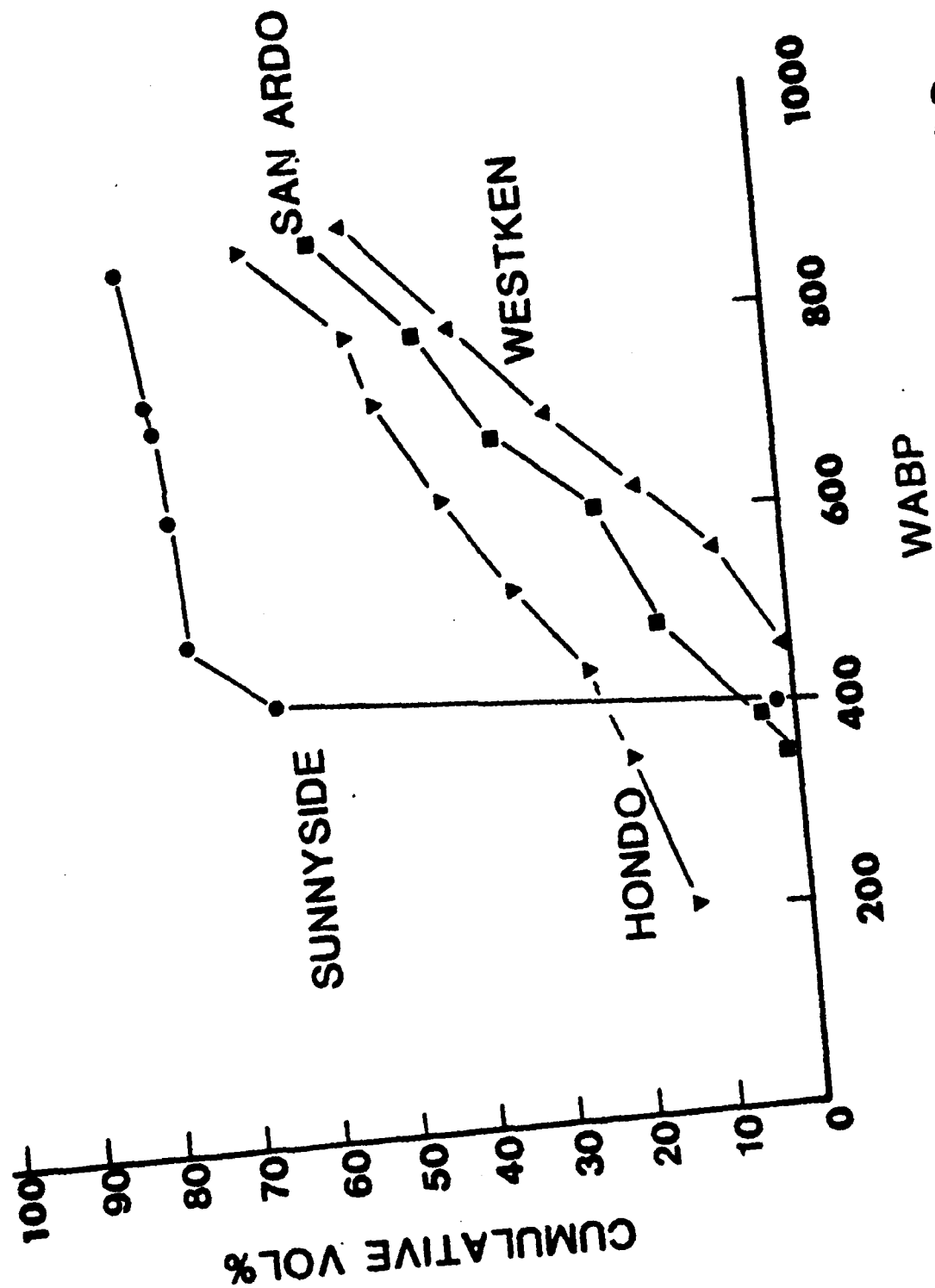
TABLE 7

## TRACE METALS EVALUATION

## WHOLE WESTKEN CRUDE

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<u>METALS DETECTED</u>	<u>CONCENTRATIONS, PPM (RANGE)</u>
IRON	488(234-894)
NICKEL	66(61-71)
VANADIUM	186(156-229)
SODIUM	829(541-1117)
POTASSIUM	168
CALCIUM	559
MAGNESIUM	130
TITANIUM	37
CHROMIUM	1
MANGANESE	10
COBALT	2
COPPER	3
ZINC	74



## CRUDE VOLUMETRIC YIELDS

FIGURE 1.

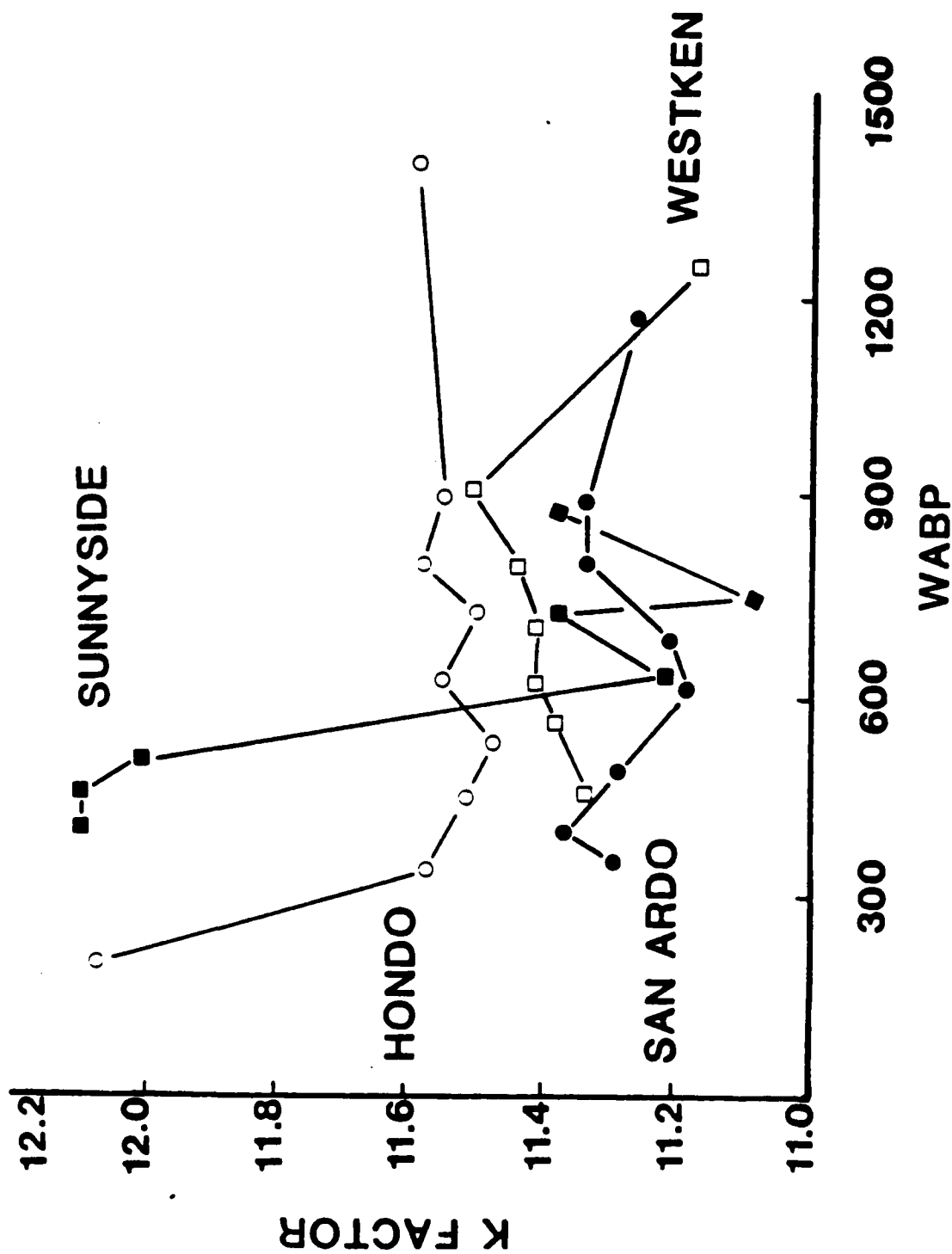
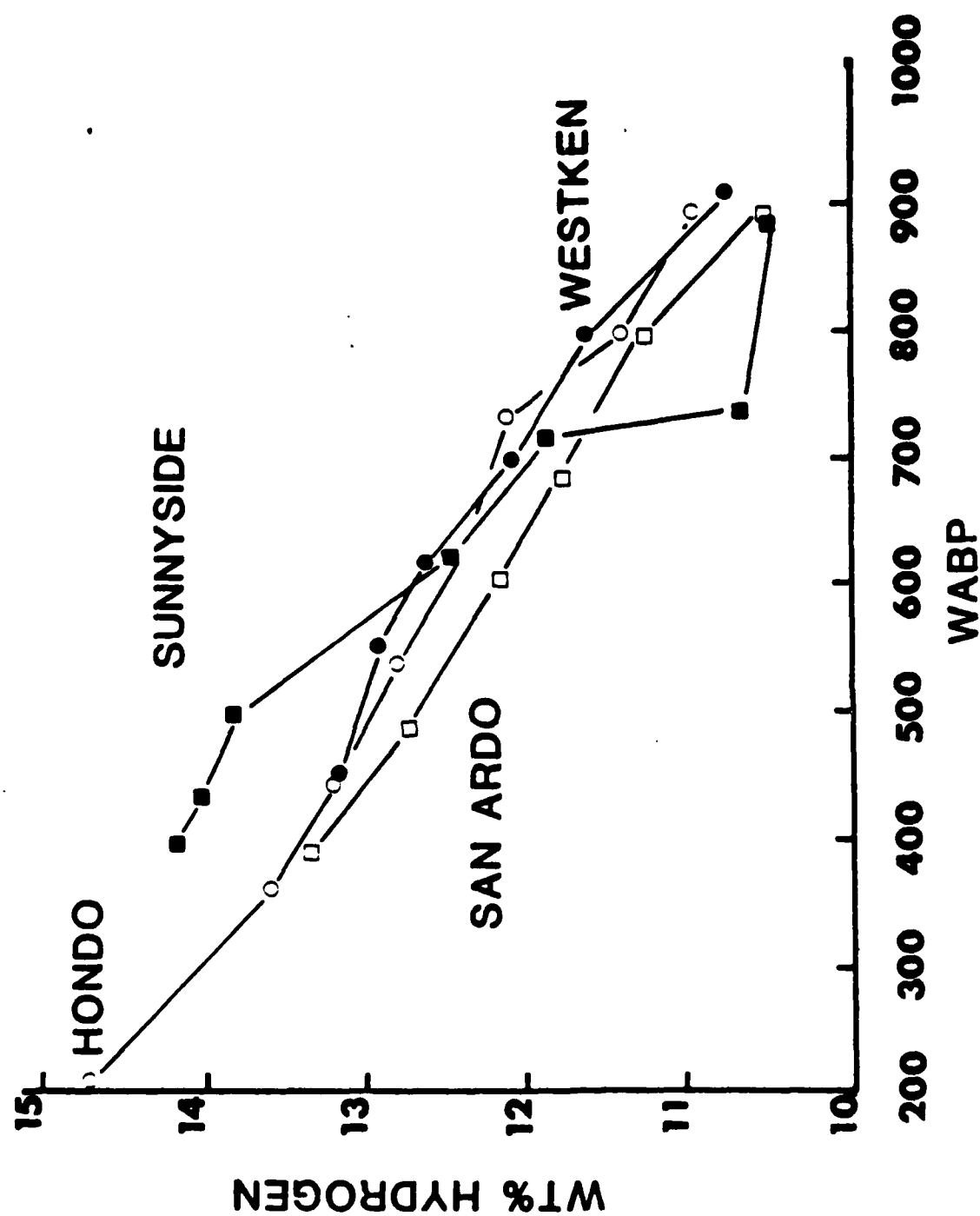


FIGURE 2. COMPONENT BOILING POINT TRENDS



## CRUDE HYDROGEN CONTENTS

FIGURE 3.

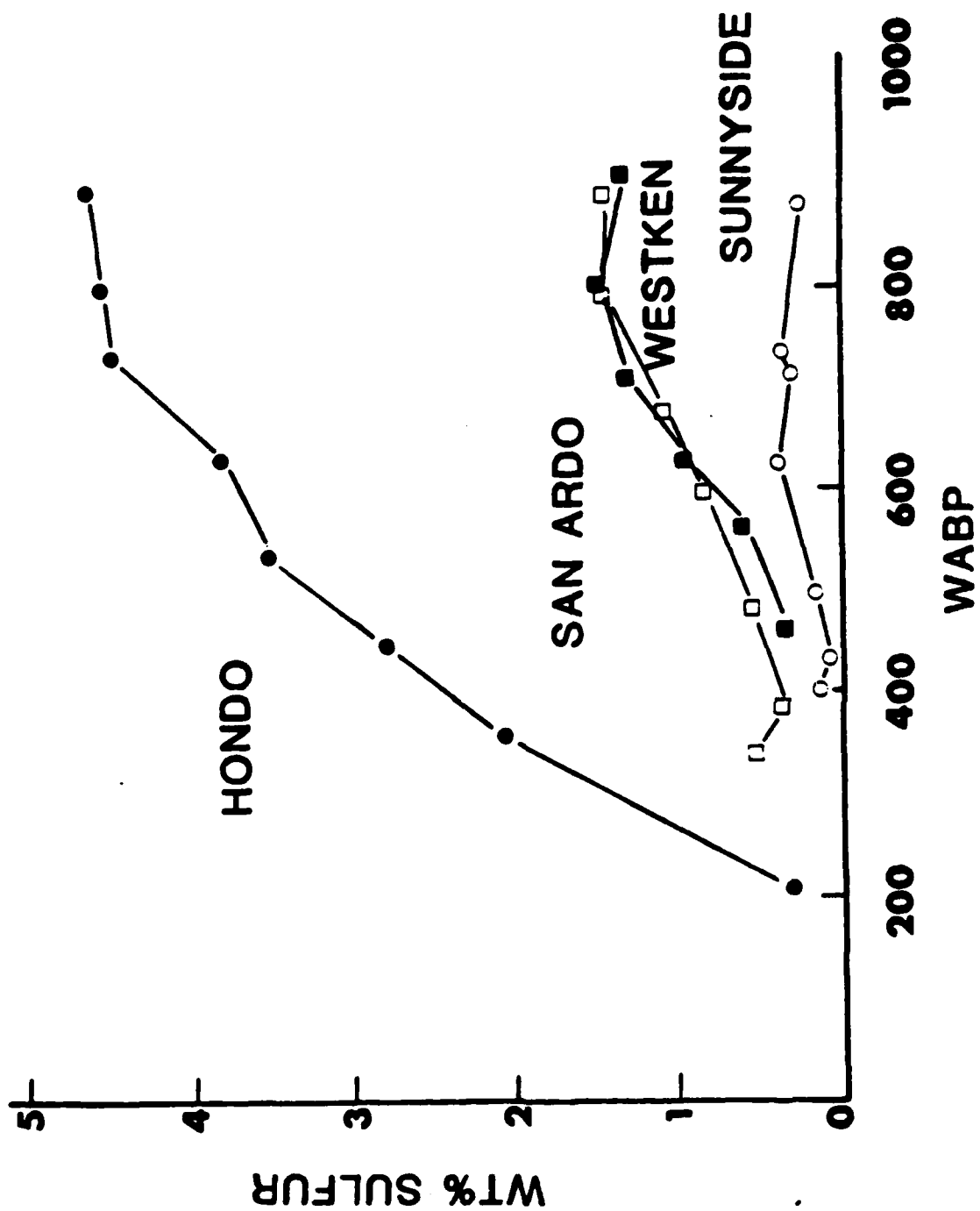


FIGURE 4 .

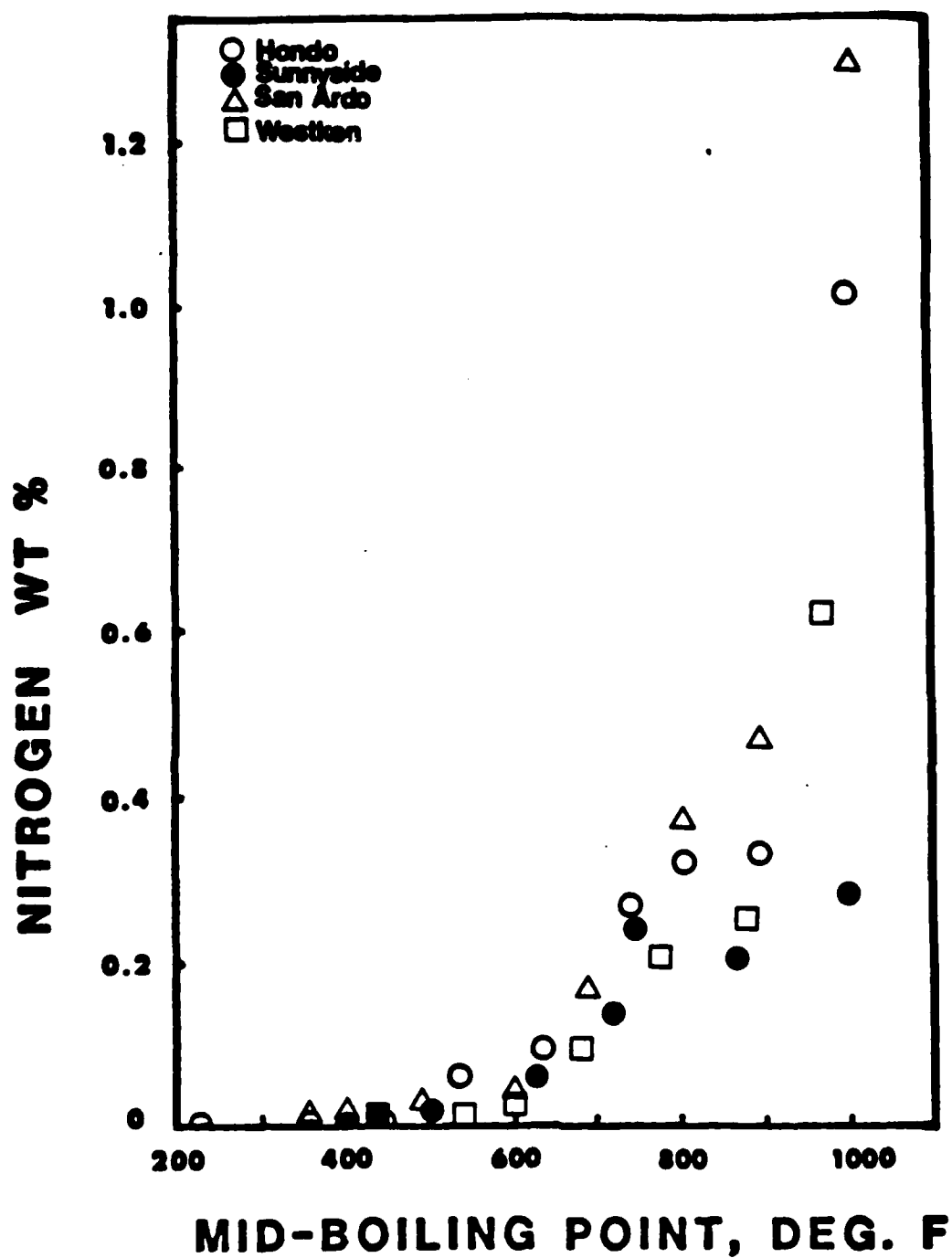


FIGURE 5. NITROGEN CONTENT  
VS  
MID BOILING POINT



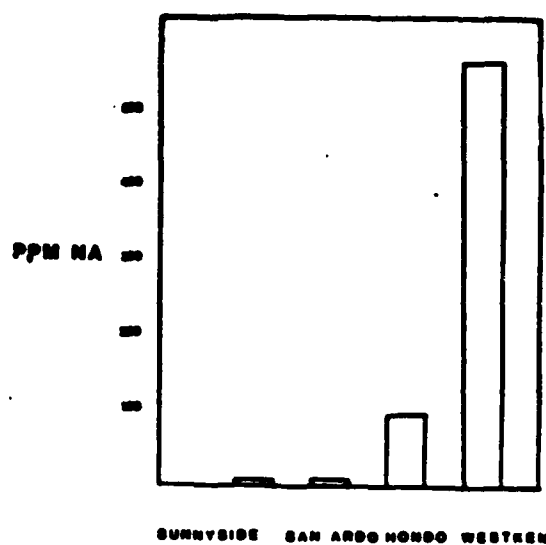


FIGURE 6. SODIUM CONTENT  
vs  
TAR SAND FEEDSTOCK

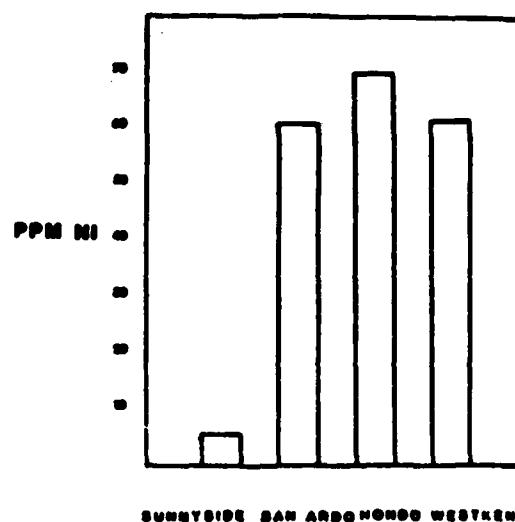


FIGURE 7. NICKEL CONTENT  
vs  
TAR SAND FEEDSTOCK

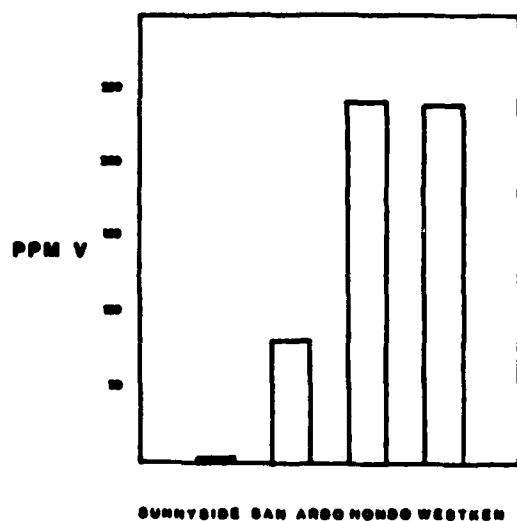


FIGURE 8. VANADIUM CONTENT  
vs  
TAR SAND FEEDSTOCK

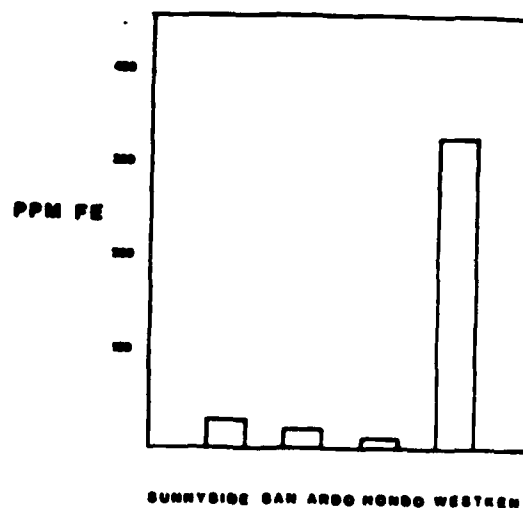


FIGURE 9. IRON CONTENT  
vs  
TAR SAND FEEDSTOCK

## Conclusions

- All crudes evaluated show high residuum contents with little or no naphtha.
- The Sunnyside data are not reliable due to variations caused by the high kerosene content.
- All crudes evaluated are very aromatic, increasing in the order Hondo < Westken < San Ardo.
- Hydrogen contents are low, particularly compared to turbine fuel hydrogen content requirements.
- Heteroatom contents vary:
  - Sulfur is very high in the Hondo crude.
  - Nitrogen contents are high in all the residual, with San Ardo being the highest.
  - Measured (non-water) oxygen levels are high in all stocks.
- Metals contents are high for all stocks; trace elements and salt are a particular problem for the Westken crude.
- Demetallization will be required for all crudes except the Sunnyside.

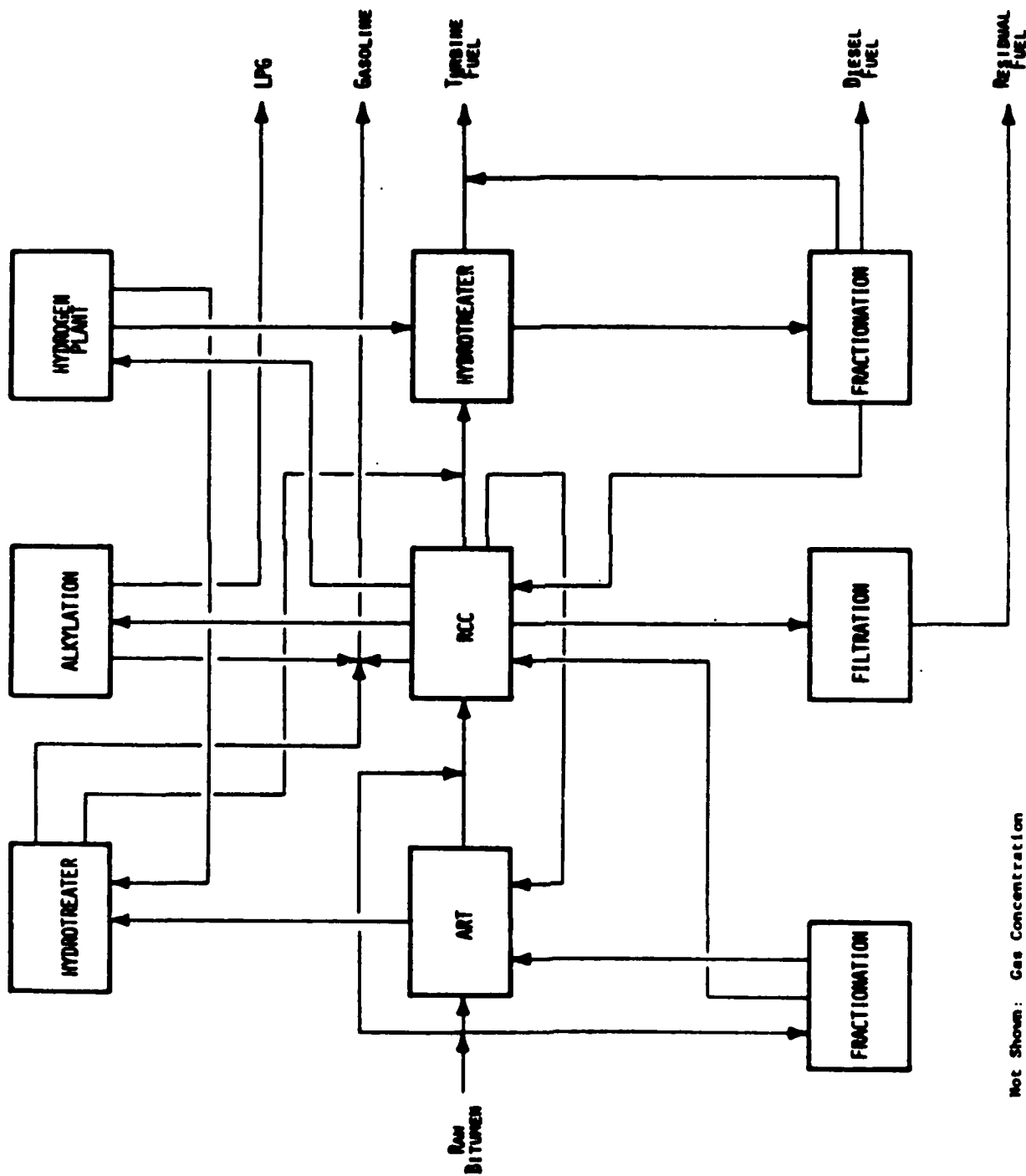
### SECTION III. PROCESSING

#### OVERALL PROCESS DESCRIPTION

The process selected for Phase II laboratory evaluation is based on Ashland's RCC process technology. This process has been developed based on laboratory, demonstration, and commercial scale equipment. A 40,000 BPD RCC unit has been successfully operated at Catlettsburg, Kentucky, since April 1983. A companion ART unit is also in use at Catlettsburg. Details of each of these processes, and recent commercial experience, have been published elsewhere<sup>10-13</sup>. Adaptations of these technologies are being developed under this program to allow processing of bitumen stocks.

The overall flow sheet for the process is shown in Figure 10. Raw bitumen feed to the complex is admixed with a refractory RCC product for dispersion and viscosity control; heavy oil (>15°API) is not diluted. After desalting, if necessary, this material is charged to the ART unit for metals removal, with an option to bypass some or all of this material to the RCC if desired. ART products are separated into fuel gas, C<sub>3</sub> + C<sub>4</sub>, naphtha, distillate, and bottoms in the associated main column and gas concentration unit.

The RCC Unit may be fed by raw feed, ART distillate, ART bottoms and/or recycle hydrogenated components ranging up to



Not Shown: Gas Concentration  
Saturate Gas Plant  
Sulfur Plant  
Offsites and Tankage

FIGURE 10 OVERALL PROCESS SCHEMATIC

900°F. The RCC module contains gas separation plus flue gas treating, and produces sour fuel gas, mixed C<sub>3</sub> + C<sub>4</sub>, C<sub>5</sub>-430 (or 330°F) gasoline, 330° or 430°F-630°F cycle oil and 630°F+ resid. Fractionation options allow cuts as deep as 900°F for recycle hydrogenation. Gasoline end point may be varied to control sulfur content of gasolines from high sulfur feedstocks. RCC gasoline and bottoms may be directed to finished product blending as needed.

Products for blending with streams other than gasoline, and for recycle, are hydrotreated. All raw ART naphtha is olefin saturated, then blended to gasoline or further hydrogenated for turbine fuel. Components for turbine or diesel fuels are hydrogenated at nominal 1800 psig conditions since significant hydrogen input is required by product specifications.

Mixed C<sub>3</sub>/C<sub>4</sub> streams are routed to HF alkylation with the ART product processed first through a small propadiene/butadiene saturation section. Hydrogen is provided either by fuel gas steam reforming or by partial oxidation of residual material. Plant fuel is provided by the remaining fuel gas or resid. For hydrogen deficient cases, all C<sub>3</sub> and C<sub>4</sub> components may also be burned as fuel or utilized in the steam reformer. The sulfur plant module includes fuel gas amine treatment, Claus-type sulfur recovery and tail gas cleanup.

Processing studies based on this flow sheet were performed on each of the four stocks. Based on literature information and feedstock characterization, lab processing was provided in the areas of:

- Desalting
- Demetallization
- Cracking
- Hydrotreating

Each of these areas is addressed in detail below.

#### DESALTING

Removal of inorganic salts from crude oils has been practiced routinely by refiners for many years, and the variety of methods for handling this problem ranges from electrostatic precipitation to chemical and mechanical separation techniques. The presence of salts in significant concentrations causes considerable refining difficulty, due mainly to:

- corrosion resulting from hydrolysis of chloride salts to HCl,
- fouling of exchanger and heater surfaces resulting from evaporative deposition of salts,
- contamination of residual products,
- catalyst deactivation in catalytic processes.

Refiners, in general, consider crude salt levels above about 10-20 pounds per thousand barrels (lbs/Mbbbls) excessive, and aim to reduce salt from this level by 90% to eliminate downstream processing problems. By comparison, salt contents as high as 900 lbs/Mbbbls have been measured in the tar sand and heavy oil samples studied here, indicating that high desalting efficiency must be attained. It is anticipated that the heavy, viscous nature of these samples will cause problems at conventional desalting conditions.

Scoping experiments were performed to determine the salt concentrations in the subject oils and to determine the conditions necessary for adequate desalting. Information derived here would be used to assist in the scale-up of the desalting process in the next phase of work. The Westken and Hondo feedstocks were judged to require desalting treatment and were chosen for experimentation.

#### Experimental Procedure

In order to perform desalting evaluations for the two feedstocks, experiments were performed in two stages. Initial screening of the two feedstocks was conducted on a small scale in glass separatory funnels. Subsequent evaluations were performed in a two liter, high-pressure "MagneDrive II" packless autoclave manufactured by Autoclave Engineers, Inc. The unit is self-contained, constructed of 316 stainless steel, with a heating jacket, feed and product

ports, and motor-driven stirrer for sample agitation. Laboratory grade sodium hydroxide was used to adjust the alkalinity of the blends used for desalting. A commercially available chemical demulsifier manufactured by Tretolite Corp., Tolad T-284, was added where noted.

### Results

The crude Hondo oil was treated as received, while the crude Westken oil was blended in equal volume with a petroleum light cycle oil. Initially, the feedstock samples were charged to a glass separatory funnel after heating the oil to 150°F. Boiling water was added to the heated oil, in a ratio of 350 mls water to 50 grams of oil. The mixture was shaken vigorously and allowed to settle for four hours with mild external heat applied. Phase separation was complete for the Hondo sample, but very little separation was evident for the Westken blend.

Following small scale screening, the Westken sample was desalted using the autoclave in order to study higher process temperature. Raw Westken tar sand bitumen was mixed in equal volume with petroleum light cycle oil. Water was added in a ratio of two parts water to one part oil, and to this mixture five mls of chemical demulsifier was added. The alkalinity of the solution was adjusted with sodium hydroxide to fall in the range of 9-11 pH. The autoclave was operated over a range of conditions from 250-350°F and 100-250PSIG pressure.



The stirring rate was held at 400RPM for 1 1/2 hours and ramped to 1000 RPM for 1/2 hour. Samples were drawn from the middle of the oil layer and analyzed for salt content.

Salt values for the raw crude showed a great deal of variation, but were generally lower for the Hondo oil than the Westken. The raw Hondo crude had about 6 lbs. of salt per thousand barrels, and virtually 100% removal was accomplished in initial screening experiments. The Westken feedstock showed highly variable salt content, ranging for multiple drum samples 35-892 lbs/Mbbls. Initial screening in glassware was inconclusive due to the very stable emulsion formed on mixing.

The autoclave experimentation was much more successful for treating the Westken feedstock. Over the range of processing severities studied, desalting efficiencies were observed ranging from 39 wt% to 99 wt% salt removal, with optimum results obtained at 350°F, 250PSIG and about three hours settling time.

#### Conclusions

- A large variation in salt content was observed for the feedstocks studied, with much higher concentrations observed in the Westken bitumen compared to the Hondo oil.
- The use of demulsifying chemicals and sodium hydroxide for pH control is extremely helpful in breaking the emulsion which readily forms in these materials.

- Maximum salt removal was observed at 350°F and 250PSIG pressure in a high pressure autoclave with three hours settling time.

#### DEMETALLIZATION

Metals, contained in varying amounts in heavy feedstocks, cause catalyst deactivation and can also catalyze unwanted reactions such as dehydrogenation. This program uses the ARTSM process, a selective vaporization/carbon rejection technology based on fluid particle contacting, to remove significant quantities of contaminant metals prior to catalyst processing.

Figure 11 schematically describes the commercial ARTSM configuration. Heavy oil is contacted with hot, regenerated sorbent at the base of the riser. Oil, sorbent, and product vapors travel in dilute phase up the riser, to the point where products and sorbent are rapidly disengaged. The spent sorbent, containing about 75% of the Ramsbottom Carbon and about 90% of the metals originally in the feed, returns to the regenerator where the carbon is burned for process heat requirements. Gaseous and liquid products are separated in a conventional manner. Key aspects of the process are low conversion, high rates of carbon rejection and demetallization, with viscosity reduction and some heteroatom removal. Process elements important to economic operation are the fluid particle treatment, which is relatively insensitive to water or

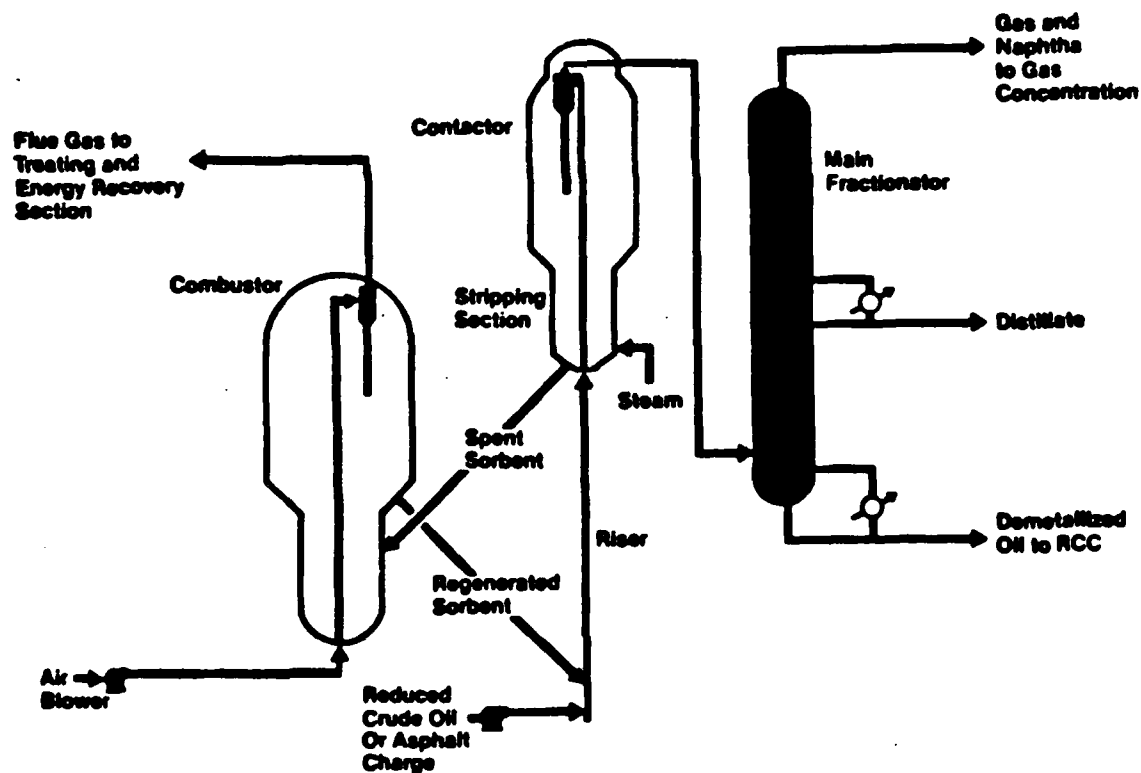


Figure 11. Process Flow Diagram--Commercial Unit Practicing ART<sup>sm</sup> Technology.

Reference: Busch, et.al., 1984 NPRA Meeting (3/25-27/84)

particulates in the feed; low pressure operation; and no requirement for external hydrogen addition.

During Phase I of this program, process analysis defined three key questions for Phase II experimentation:

- Feedstock pre-separation
- Optimum diluent type and quantity
- Specific crude response and product properties

Each of these elements were addressed, and the results are summarized below.

#### Feedstock Pre-Separation

Major metals and carbon-containing contaminants in essentially all petroleum-type materials are contained in the vacuum (>1000°F) residue and in particular in the asphaltene concentrate. Processing of just this fraction, or a further separated asphaltene concentrate, could provide advantages in terms of smaller unit size, lower utilities costs, and no thermal degradation of the separated components. However, disadvantages to this approach are the capital and operating requirements of the separation, plus the mechanical requirement of dilution for very heavy, viscous feeds. The preferred route would be a tradeoff between these elements.

Westken crude was selected for this analysis. While use of the Westken limits information on the effects of distillate

(<630°F) separation, its high metals and carbon contents make an excellent analysis tool. Crude Westken was separated by three methods:

1. Atmospheric fractionation
2. Vacuum fractionation
3. Solvent deasphalting

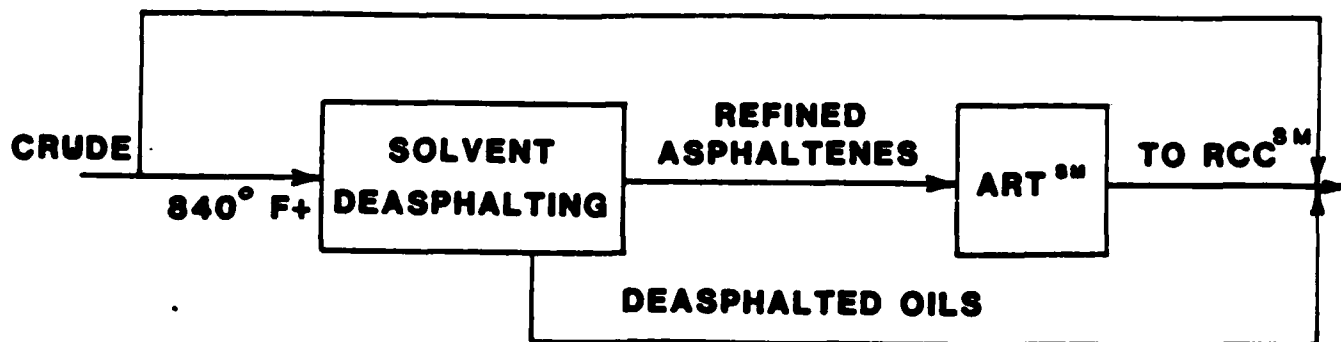
These routes are shown schematically in Figure 12.

Properties of the raw Westken feedstock for evaluation are shown in Table 8. Because of the viscous nature of these materials a petroleum LCO from commercial RCC operations was used for dilution during testing. Properties of this LCO are also shown in Table 8.

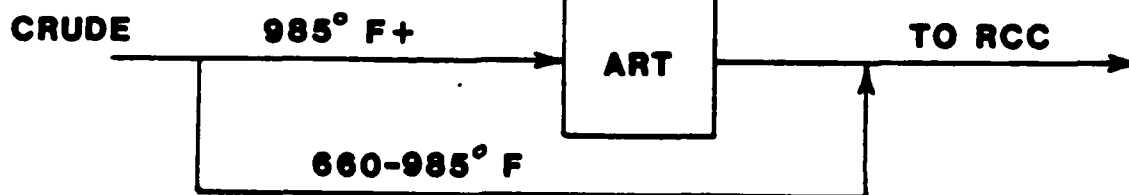
Table 9 presents response data for tests on a fixed fluidized system including diluent. Consistent trends are noted in coke and 630°F+ yields, but gas yields for the asphaltene tests are very low. Calculated diluent-free yields from each feedstock based on these data are shown in Table 10. Table 11 summarizes these data based on whole crude i.e., the ART yields plus material separated prior to the ART module. Overall, on a whole crude basis, net coke produced decreases with the amount of material processed, but only by a slight amount. Total liquid yields (C<sub>3</sub>+) are similar, except for a 2-3% advantage to the asphaltene case. In fact, the yields (at least for the fractionation cases) are remarkably

- Solvent Deasphalting

660-840° F



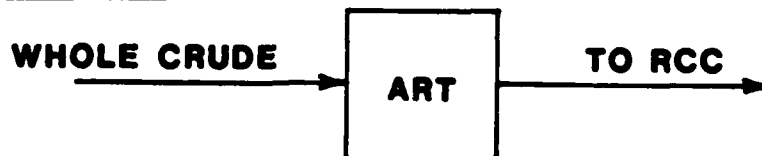
- Vacuum Fractionation



- Atmospheric Fractionation



- No Preseparation



**Figure 12. Preseparation Alternatives**

Table 8

## Properties of Materials Utilized in Diluent Optimization Studies

	Diluent	Westken Fractions			
		Whole Crude	650°F+ Atmospheric Bottoms	985°F+ Vacuum Bottoms	Refined Asphaltenes
Yield, % Crude	-	-	87.3	52	17.8
API Gravity	17.3	10.4	7.5	0.9	-
Elemental Analyses, Wt. %					
Hydrogen	10.1	11.0	-	10.35	7.7
Nitrogen	0.12	0.23	0.32	0.61	1.7
Sulfur	1.28	1.66	1.57	1.94	2.46
Elemental Analyses, ppm					
Iron	nil	335	-	1500	-
Nickel	nil	63	-	114	-
Vanadium	nil	229	-	458	-
Ramsbottom Carbon	-	11.0	-	15.3	-
Component Analysis, wt%:					
Asphaltenes	-	20.3	22.1	41.5	99.2
Saturates	25.4	28.0	23.8	11.1	-
Aromatics	72.1	24.1	30.2	16.7	-
Polars	2.5	27.6	23.9	30.7	-

Table 9

ART Yields For Separated Westken  
Feeds, As Processed

Feed	Diluent	Whole Crude	650°F+ Atmospheric Bottoms	985°F+ Vacuum Bottoms	Refined Asphal- tenes
Diluent Added, % w.	100	30	25*	30	50
Test No.	1420-51	1420-23	1420-32	1420-53	1420-47
Operating Conditions:					
Temperature, °F	902	921	900	901	903
c/o Ratio	4.0	4.3	4.3	4.2	4.7
WHSV	24	24	24	24	24
Yield Structure, Wt.% of feed (Normalized)					
Hydrogen	0.02	0.18	0.22	0.40	0.17
Methane	0.00	0.41	0.76	1.19	0.68
Ethane + Ethylene	0.11	1.23	1.74	1.83	0.08
Propane	0.04	0.53	0.84	0.92	0.04
Propylene	0.05	0.70	0.90	0.89	0.04
Isobutane	0.00	0.00	0.00	0.09	0.00
Normal Butane	0.00	0.25	0.39	0.53	0.06
Butenes	0.01	0.57	0.75	0.92	0.08
C <sub>5</sub> -430°F	9.75	5.58	5.63	13.45	8.74
430-630°F	66.14	34.34	31.66	31.30	37.77
630°F+	22.63	49.91	49.96	37.64	30.01
Coke	1.25	6.30	7.55	10.84	22.34

\*using a narrow-cut, 500-600°F diluent

Note: See Figure 12 for definition of process streams and options.



Table 10  
Calculated ART Yield Structures for Fractions  
Based on Diluent Free Feedstock

<u>ART Yields, wt.%</u>	<u>Whole Westken</u>	<u>650°F+ Westken</u>	<u>985°F+ Westken</u>	<u>Refined Asphaltenes</u>
Dry Gas	2.54	3.56	4.83	1.73
C <sub>3</sub> - C <sub>4</sub> 's	2.89	3.76	4.74	0.34
C <sub>5</sub> - 430°F	3.79	6.60	15.04	7.73
430 - 630°F	20.71	11.48	16.37	9.40
630°F+	61.60	64.85	44.07	37.39
Coke	8.46	9.74	14.95	43.43

Table 11  
Calculated Crude Basis Yields for ART Processed  
Fractions Plus Pre-Separated Components

Basis: Crude = 100%

<u>Whole Crude Yields, wt.%</u>	<u>Fraction Processed In the ART Unit</u>			
	<u>Whole Westken</u>	<u>650°F+ Westken</u>	<u>985°F+ Westken</u>	<u>Asphaltenes</u>
Dry Gas	2.5	3.0	2.5	0.3
C <sub>3</sub> - C <sub>4</sub> 's	2.9	3.2	2.5	0.1
C <sub>5</sub> - 430°F	3.8	5.6	7.9	1.4
430 - 630°F	20.7	24.3	22.9	16.2
630°F+	61.6	55.6	56.4	74.4
Coke	8.5	8.3	7.8	7.6
Total C <sub>3</sub> +Liquids	89.0	88.7	89.7	92.1

similar. Considering utilities, capital investment, and plant complexity factors, separation of the ART feed prior to processing cannot be justified for this feedstock.

#### Diluent Optimization

A diluent may be required for ART processing due to the nature of the feed. In general, the advantages of using a diluent include improving the flow properties of the feed by lowering viscosity and pour point, improving contact of the feedstock with the sorbent for better feed distribution while minimizing diffusional effects, reducing carbon-on-sorbent by lowering overall feed resid content, and potentially improving feedstock reaction selectivity by addition of hydrogen donors to quench free radicals prior to polymerization. The disadvantages of diluent usage are reducing total capacity of a given unit and loss of yield by conversion of some portion of the diluent recycle. In general, for economic reasons, the diluent should be process-derived.

From practical and chemical considerations, recycle RCC light cycle oil (LCO) was postulated to be nearly an optimum diluent. In addition to being process-derived, this stream contains significant quantities of one- and two-ring aromatic compounds which are very stable to this type of processing. In order to simulate RCC LCO produced from these materials, a commercial RCC LCO sample from petroleum operation was

obtained (Table 12). For optimization purposes, this material was fractionated into narrow boiling cuts, 400-500°F and 500-600°F, and each was tested as a diluent.

Finally, the option of providing a hydrogen donor as diluent was tested by hydrogenating the same LCO at conditions estimated to maximize formation of tetralin-type molecules, Table 13. The composite product from this operation (completed in four runs) was fractionated into 400-500°F and 500-600°F concentrates corresponding to the earlier raw fractions. Properties of these products are shown in Table 13 as well.

The bitumen feedstock for all diluent evaluations was the 650°F+ Westken for which properties were presented in Table 8. The sorbent used was a commercial equilibrium sample with 4100 ppm nickel, 11300 ppm vanadium, and 6900 ppm iron.

All tests were performed in a fixed-fluidized bed reactor operating in a cyclic manner for feed, purge, regeneration, and purge sequences. Nominal conditions for all tests were 900°F, 4:1 catalyst-to-oil ratio, and 24 WHSV based on prior unit characterization with petroleum feedstocks.

Results from the diluent tests are summarized in Tables 14-18. In general, the heavier diluent makes more coke but less naphtha than the lighter diluent, and has lower total

Table 12  
Experimental Diluent Properties

	<u>Raw<sup>2</sup></u> <u>LCO</u>	<u>Raw<sup>1</sup></u> <u>400-500</u>	<u>Raw<sup>2</sup></u> <u>500-600</u>	<u>Hydro-</u> <u>treated</u> <u>400-500</u>	<u>Hydro-</u> <u>treated</u> <u>500-600</u>
°API	17.3	25.2	19.3	26.0	23.8
Elemental, wt.% (ppm)					
Hydrogen	10.1	10.5	10.0	11.3	11.2
Sulfur	1.07	0.48	1.04	(44)	(4)
Nitrogen	0.12	(377)	(420)	(99)	(339)
Saturates, wt.%(LV%)	25.4	(11.2)	28.9	6.5	-
Olefins, wt.%(LV%)	-	(8.9)	-	2.6	-
Aromatics, wt.%(LV%)	72.1	(79.9)	71.1	90.9	-

1) Compound types by FIA

2) Compound types by mass spectrometry

Table 13  
Hydrotreating RCC Cycle Oil

PERIOD	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>TOTAL</u>
OPERATING CONDITIONS					
Temperature, °F	676	676	675	685	678
Pressure, PSIG	879	874	854	850	864
LHSV, Hr <sup>-1</sup>	2.04	2.06	2.08	2.07	2.06
H <sub>2</sub> Rate, SCFB	3030	3005	2900	3070	3000
MATERIAL BALANCE					
Weight Percent of Feed					
NH <sub>3</sub>	0.14	0.13	0.12	0.14	0.13
H <sub>2</sub> S	0.56	0.25	0.46	0.22	0.37
C <sub>2</sub>	0.02	0.01	0.01	0.63	0.17
C <sub>3</sub>	0.01	0.01	0.01	0.01	0.01
C <sub>4</sub>	-	0.02	0.01	0.02	0.01
C <sub>5</sub> + Stabilized Liquid	100.26	100.52	100.55	100.15	100.41
Hydrogen					
Consumption, SCFB	670	695	750	770	725
Liquid Product Properties					
°API	23.8	23.6	23.4	23.6	
% Hydrogen	11.0	11.1	11.1	11.1	
% Sulfur	0.16	0.21	0.20	0.17	
Nitrogen, ppm	100	105	170	157	

Table 14

Observed Westken ART Yields, Wt. %, When Using  
400-500°F RCC Cycle Oil Diluent

	Tar Proportions, Wt. %			
	<u>0</u>	<u>50</u>	<u>75</u>	<u>100</u>
Dry Gas	0.50	1.40	1.62	2.30
C <sub>3</sub> - C <sub>4</sub> 's	0.55	1.20	1.46	2.27
C <sub>5</sub> - 430°F	19.51	15.93	12.41	8.63
430 - 630°F	77.91	45.59	26.59	15.26
630°F+	0.98	30.83	48.67	63.58
Coke	0.55	5.06	9.25	7.98
Conversion	3.8	16.0	21.2	21.2

Table 15

Weight Percent Westken ART Yields, When Using  
Raw 400-500°F RCC Cycle Oil Diluent,  
Corrected for Diluent Content

	Tar Proportions, Wt. %		
	<u>50</u>	<u>75</u>	<u>100</u>
Dry Gas	2.30	1.99	2.30
C <sub>3</sub> - C <sub>4</sub> 's	1.85	1.76	2.27
C <sub>5</sub> - 430°F	12.35	10.04	8.63
430 - 630°F	13.27	9.48	15.26
630°F+	60.68	64.56	63.58
Coke	9.57	12.15	7.98
Conversion	28.3	27.0	21.2

Table 16

Westken ART Yields, Wt. %, When Using  
500-600°F RCC Cycle Oil Diluent

	Tar Proportions, Wt. %			
	<u>0</u>	<u>50</u>	<u>75</u>	<u>100</u>
Dry Gas	0.18	1.41	2.72	2.30
C <sub>3</sub> - C <sub>4</sub> 's	0.22	1.74	2.88	2.27
C <sub>5</sub> - 430°F	1.13	3.17	5.23	8.63
430 - 630°F	92.20	55.22	31.66	15.26
630°F+	5.29	30.55	49.96	63.58
Coke	0.99	7.93	7.55	7.98
Conversion	2.5	14.2	18.3	21.2

Table 17

Weight Percent Westken ART Yields When Using  
500-600°F RCC Cycle Oil Diluent,  
Corrected for Diluent Content

	Tar Proportions, Wt. %		
	<u>50</u>	<u>75</u>	<u>100</u>
Dry Gas	2.64	3.56	2.30
C <sub>3</sub> - C <sub>4</sub> 's	3.26	3.76	2.27
C <sub>5</sub> - 430°F	5.21	6.60	8.63
430 - 630°F	18.24	11.48	15.26
630°F+	55.81	64.85	63.58
Coke	14.87	9.74	7.98
Conversion	25.9	23.6	21.2

conversion. The actual magnitude of the difference is small, however. Comparison of these data with results from full-range cycle oil, Tables 19 and 20, demonstrates no advantage for the narrow cut diluents. Accordingly, the full-range cycle oil diluent was recommended for use.

Tables 14-18 also demonstrate the effect of diluent quantity on yields. In general, additional diluent leads to more coke and thermal naphtha. These data suggest that diluents be limited to the lowest possible level consistent with good distribution and mechanical operation of the unit.

Hydrotreated diluents were tested only at the 50% level, Table 18. Comparison with raw diluents shows that hydro-treatment produces less gas, but more coke, than the raw diluent. The yields for both diluents are roughly comparable, although an expected reduction in coke yield was not observed with use of hydrotreatment.

Overall, full-range diluents were recommended for use at levels as low as possible. While hydrogenation of the diluent did not show expected benefits in ART processing, this option was shown to be acceptable if justified in other steps.



Table 18  
Observed Westken Art Yields, Wt. %,   
with 50% Diluent

	<u>400-500°F Diluent</u>		<u>500-600°F Diluent</u>	
	<u>Hydrotreated</u>	<u>Raw</u>	<u>Hydrotreated</u>	<u>Raw</u>
Dry Gas	0.59	1.40	0.65	1.41
C <sub>3</sub> + C <sub>4</sub>	0.15	1.20	0.55	1.74
C <sub>5</sub> - 430°F	14.46	15.93	4.19	3.17
430 - 630°F	45.78	45.59	54.56	55.22
630°F+	31.62	30.83	31.77	30.55
Coke	7.41	5.06	8.30	7.93

### Feedstocks

The four crude stocks were further evaluated for specific ART response on a nominal 10 pounds per hour circulating pilot unit with continuous sorbent regeneration. Operating conditions and unit parameters were determined based on the lab screening studies designed previously.

#### 1. Westken

Westken bitumen required dilution for ART processing. Based on laboratory fixed-fluidized bed data, a full-range non-hydrotreated LCO diluent was selected. Initial ART operating efforts at 30% dilution (Table 19) resulted in a poor yield pattern, resulting in the decision to operate at a higher dilution level of 50%. After mechanical problems were corrected, which could have caused some of the operating difficulty of the 70/30 mixture, an acceptable mass balance test was performed on the 50/50 mixture.

Products from these tests were composited and fractionated into the products shown in Table 20; these products still contain significant quantities of LCO diluent. Excellent carbon and metals removals were obtained.

Table 19

ART Processing of Westken  
Crude On A Pilot Circulating Unit

Test, 1374-	11	13	23	52
% Diluent*	100	100	30	50
Operating Conditions:				
Temperature, °F	898	905	908	902
c/o Ratio	18	16	35	15.6
Riser Water, % feed	11.6	7.9	22.6	15.0
Yields, Wt.% Feed (normalized)				
Hydrogen Sulfide	0.0	0.0	0.4	0.2
Hydrogen	0.1	0.1	0.2	0.2
Methane	0.0	0.0	0.5	0.8
Ethane + Ethylene	0.6	0.8	1.6	1.8
Propane	0.1	0.1	0.4	0.4
Propylene	0.4	0.5	1.2	1.1
Isobutane	0.0	0.0	0.0	0.0
Normal Butane	0.0	0.0	0.1	0.1
Butenes	0.3	0.3	1.0	0.9
C <sub>5</sub> - 430	6.2	6.4	8.5	8.3
430 - 630	61.5	61.3	29.2	41.3
630+	24.3	23.8	32.3	34.5
Coke	6.4	6.7	24.6	10.6

\*Weight percent diluent in the combined feed.

Table 20

## Product Properties for ART Treated Westken Crude

	<u>I-200</u>	<u>200-500</u>	<u>500+°F</u>
Yield, Wt%	3.47	12.51	84.02
API	50.2	26.8	12.5
Elemental Analysis			
Hydrogen, Wt%	-	10.57	9.80
Nitrogen, Total, ppm(Wt%)	104	211	(0.17%)
Nitrogen, Basic, ppm(Wt%)	53	91	(0.05%)
Sulfur, Wt%	0.10%	0.89%	1.51%
FIA, Vol.%			
Saturates	-	18.9	-
Olefins	-	14.7	-
Aromatics	-	66.4	-
HPLC, Wt.%			
Saturates	-	-	25.9
Mono Aromatics	-	-	5.4
Di Aromatics	-	-	29.9
Tri Aromatics	-	-	32.1
Polars	-	-	5.7
Asphaltenes	-	-	0.8
Distillation: 5 Wt%	-	317°F	480°F
(D-2887) 10	-	354	503
30	-	424	567
50	-	450	635
70	-	477	712
90	-	492	932
95	-	504	1001 at 94%
RVP, psi	10.0	0.1	-
Metals (ppm) Ni	-	-	1
Va	-	-	3
Na	-	-	1
Fe	-	-	1
Viscosity, cp at 140°F	-	1.53(100°)	7.71
210°F	-	1.13(140°)	3.09
Bromine No.	-	23.2	-
MAV	-	7.6	-
Ramsbottom Carbon, Wt%	-	-	2.21
Phenols, ppm	-	190	-

## 2. Hondo

The Hondo crude was processed as-received, even though the material contained significant quantities of virgin naphtha and distillate. These light materials negated any diluent needs. The 18° API gravity crude was upgraded to a 27.2° API syncrude.

Seven ART tests were performed, with four having acceptable material balance closures (Table 21). The most noteworthy features were the high H<sub>2</sub>S yield, due to high feed sulfur, and high naphtha yield due to the high virgin naphtha in the feed. Coke yields were higher than desired, primarily due to present characteristics of the experimental unit. Commercial coke yields would be 3-5% lower.

Material from all seven tests were composited, with a total of 229 pounds of product recovered and fractionated. Product properties, Table 22, show an overall improvement compared to the feed. Less metal was removed than expected for unknown reasons. Composite product sulfur is significantly lower than the feed (3.75% vs. 5.02%).

## 3. San Ardo

Whole San Ardo crude was ART treated without dilution; the 14.0° API crude was processed to a composite syncrude gravity of 20.9° API. Six tests were performed, with four having acceptable mass closure (Table 23). Only high coke yields

Table 21

ART Processing of Hondo Crude

Test No.	163	160	155	139
Operating Conditions:				
Temperature, °F	909	924	939	942
c/o Ratio	15	10	24	32
Water, % feed	7.7	5.8	10.9	8.3
Yields, Wt.% of Feed (Normalized)				
Hydrogen Sulfide	1.6	1.2	1.3	0.9
Hydrogen	0.3	0.3	0.2	0.2
Methane	1.4	1.3	0.7	1.0
Ethane + Ethylene	2.7	2.6	1.4	1.9
Propane	1.0	1.1	0.5	0.7
Propylene	1.9	1.8	1.0	1.3
Isobutane	0.1	0.1	0.0	0.2
Normal Butane	0.4	0.4	0.2	0.2
Butenes	1.7	1.4	0.8	0.4
C <sub>5</sub> -430°F	27.7	31.5	22.9	28.1
430-630°F	18.9	19.0	19.1	18.3
630°F+	30.2	29.4	39.1	33.4
Coke	12.3	10.0	12.7	12.1

Table 22

HONDO PRODUCTS FROM ART PROCESSING

	<u>I-200°F</u>	<u>200-500°F</u>	<u>500+°F</u>
Yield, Wt%	13.33	19.94	66.73
API	61.3	40.2	13.9
Elemental Analysis			
Hydrogen, Wt%	-	12.74	10.62
Nitrogen(Total), ppm(Wt%)	-	-	-
Nitrogen(Basic), ppm(Wt%)	85	(0.03)	(0.23)
Sulfur, Wt%	0.94	2.76	4.61
FIA, Vol.%			
Saturates	-	49.4	-
Olefins	-	19.9	-
Aromatics	-	30.7	-
HPLC, Wt.%			
Saturates	-	-	27.3
Mono Aromatics	-	-	14.4
Di Aromatics	-	-	10.8
Tri Aromatics	-	-	32.6
Polars	-	-	12.2
Asphaltenes	-	-	2.6
Distillation: 5 Wt%	-	247°F	503°F
(D-2887) 10	-	272	534
30	-	324	633
50	-	371	733
70	-	413	843
90	-	465	985
95	-	481	1011 at 93%
RVP, psi	6.2	0	
Metals (ppm) Ni	-	-	17
Va	-	-	59
Na	-	-	4
Fe	-	-	11
Viscosity in cp at 140°F	-	0.88	-
210°F	-	-	8.13
Bromine No.	-	52.5	-
MAV	-	17.1	-
Ramsbottom Carbon, Wt%	-	-	5.36
Phenols, ppm	-	230	-

\*Due to volatile nature, unable to obtain accurate results.

Table 23

Circulating Unit ART Results for San Ardo Crude

Test No.	166	172	181	185
Operating Conditions:				
Temperature, °F	939	925	936	912
c/o Ratio	17.7	16.2	20.3	13.6
Riser Water, % feed	8.6	10.7	17.1	17.4
Yields, Wt.% of Feed (Normalized)				
Hydrogen Sulfide	0.6	0.4	0.6	0.6
Hydrogen	0.3	0.3	0.4	0.3
Methane	1.1	1.3	1.7	1.3
Ethane + Ethylene	2.1	1.6	2.7	2.4
Propane	0.7	0.5	0.8	0.8
Propylene	1.5	1.2	2.0	1.6
Isobutane	0.1	0.0	0.1	0.1
Normal Butane	0.2	0.1	0.2	0.2
Butenes	0.4	1.0	1.5	1.3
C <sub>5</sub> -430°F	17.2	14.1	16.3	20.9
430-630°F	20.4	23.4	21.3	22.6
630°F+	41.2	42.4	37.4	35.0
Coke	14.2	13.8	15.0	13.0



were unusual in these tests; again these cokes are ascribed to the present configuration of the experimental unit.

Fractionation was performed on 187 pounds of composite material to arrive at the products shown in Table 24. Metal and asphaltene removal at expected levels were observed. The total syncrude shows lower sulfur and nitrogen (1.43%, 0.59%) than the crude (1.83%, 0.91%).

#### 4. Sunnyside

As-received Sunnyside (with kerosene diluent) was processed in five ART tests, of which four had acceptable mass closures. Two further tests were performed on a kerosene alone to allow elucidation of actual Sunnyside responses (Table 25 and 26). Properties of the products of fractionation of Sunnyside ART are shown in Table 27.

Because of the highly dilute nature of the Sunnyside product, ART processing was judged to be not required in a commercial process. The metals levels encountered in this material are readily handled in the RCC unit. Further sample preparation for this feed was based on an RCC-only product.

Table 24

San Ardo Products From Art Processing

	<u>I-200°F</u>	<u>200-500°F</u>	<u>500+°F</u>
Yield, Wt%	4.86	21.09	74.5
API	53.9	36.5	13.7
Elemental Analysis			
Hydrogen, Wt%	-	12.53	10.37
Nitrogen (Total), ppm(Wt%)	260	704	(0.78)
Nitrogen (Basic), ppm(Wt%)	85	(0.05)	(0.30)
Sulfur, Wt%	0.60	0.97	1.62
FIA, Vol.%			
Saturates	-TOO DARK	TO DO	-
Olefins	-	-	-
Aromatics	-	-	-
HPLC, Wt.%			
Saturates	-	-	30.3
Mono Aromatics	-	-	14.0
Di Aromatics	-	-	9.5
Tri Aromatics	-	-	31.0
Polars	-	-	12.9
Asphaltenes	-	-	2.2
Distillation: 5 Wt%	-	248°F	502°F
(D-2887) 10	-	282	528
30	-	359	621
50	-	406	710
70	-	443	804
90	-	484	903
95	-	505	933
RVP, psi	6.3	3	-
Metals (ppm) Ni	-	-	8
Va	-	-	14
Na	-	-	5
Fe	-	-	1
Viscosity, cp at 140°F	-	0.99	-
210°F	-	-	12.1
Bromine No.	-	47.2	-
MAV	-	25.4	-
Ramsbottom Carbon, Wt%	-	-	5.10
Phenols, ppm	-	240	-

Table 25

Sunnyside ART Yield Summary

FEED: SUNNYSIDE TAR SANDS

SORBENT: EQUILIBRIUM ARTCAT

TEST NO. B1359-	120	123	130	132	134
OPERATING CONDITIONS					
Riser Temperature, °F	950	924	922	950	910
Cat/Oil Weight Ratio	21.7	12.5	11.6	14.9	12.8
Conversion, Vol%	66.35	65.7	51.9	58.1	59.8
H <sub>2</sub> O (Wt% of Feed)	9	10	11	10	10
Wt Recovery, Wt%	100.96	95.8	80.8	99.8	95.6
WT% COMPONENT YIELDS					
Methane	0.81	0.73	0.42	0.51	0.24
Ethane & Ethylene	1.69	1.08	1.18	1.21	0.89
Propane	0.24	0.19	0.19	0.20	0.14
Propylene	1.44	0.97	0.90	0.99	0.76
C <sub>4</sub> Saturates	0.40	0.41	0.10	0.25	0.28
C <sub>4</sub> Olefins	3.80	3.67	0.73	2.22	2.45
C <sub>5</sub> -430°F	46.85	49.16	37.94	44.04	46.66
430-630	31.72	32.73	48.36	43.44	39.18
630°F+	5.24	4.89	4.48	2.57	4.98
Coke	7.64	6.02	5.61	4.49	4.34
H <sub>2</sub> , SCFB	94	86	51	51	43

Table 26

ART Sunnyside Response on a Kerosene - Free Basis

FEED:	SUNNYSIDE	KEROSENE	CALCULATED SUNNYSIDE BITUMEN YIELD
TEST NO. B1359-	123	104	
OPERATING CONDITIONS			
Riser Temp., °F	924	926	
Cat/Oil Wt. Ratio	12.5	39.6	
Conversion, Vol%	65.7	65.8	57.18(Wt%)
H <sub>2</sub> O (Wt% of Feed)	10	9	
Wt. Recovery, Wt%	95.8	98.8	
WT% COMPONENT YIELDS			
Methane	0.73	0.32	1.70
Ethane & Ethylene	1.03	0.44	2.42
Propane	0.19	0.07	0.47
Propylene	0.97	0.66	1.70
C <sub>4</sub> Saturates	0.41	0.15	1.02
C <sub>4</sub> Olefins	3.57	0.84	10.33
C <sub>5</sub> -430°F	49.16	57.57	29.69
430-630	32.73	35.39	26.67
630°F+	4.89	0.09	16.19
Coke	6.02	4.41	9.82

FEED:	SUNNYSIDE	KEROSENE	CALCULATED SUNNYSIDE BITUMEN YIELD
TEST NO. B1359-	120	102	
OPERATING CONDITIONS			
Riser Temp., °F	950	950	
Cat/Oil Wt. Ratio	21.7	19.8	
Conversion, Vol%	66.35	67.78	53.26(Wt%)
H <sub>2</sub> O (Wt% of Feed)	9	10	
Wt. Recovery, Wt%	101	100.5	
WT% COMPONENT YIELDS			
Methane	0.81	0.51	1.56
Ethane & Ethylene	1.69	0.98	3.45
Propane	0.24	0.13	0.52
Propylene	1.44	1.22	2.04
C <sub>4</sub> Saturates	0.4	0.20	0.90
C <sub>4</sub> Olefins	3.80	1.40	4.83
C <sub>5</sub> -430°F	46.85	57.52	22.75
430-630°F	31.72	33.38	28.82
630°F+	5.24	0.09	17.88
Coke	7.64	4.53	12.29

Table 27

Sunnyside Product From ART Processing

	<u>I-200°F</u>	<u>200-500°F</u>	<u>500+°F</u>
Yield, Wt%	1.61	87.17	11.21
API	67.4	43.9	19.6
Elemental Analysis:			
Hydrogen, Wt%	-	13.96	11.70
Nitrogen, (Total) ppm(Wt%)	*	19	(.25)
Nitrogen, (Basic) ppm(Wt%)	*.01%	11	(.15)
Sulfur, ppm (wt. %)	*	198 ppm	(.35)
FIA, Vol.%			
Saturates	-	82.9	-
Olefins	-	6.7	-
Aromatics	-	10.4	-
HPLC, Wt.%			
Saturates	-	-	45.9
Mono Aromatics	-	-	10.7
Di Aromatics	-	-	9.6
Tri Aromatics	-	-	23.9
Polars	-	-	8.5
Asphaltenes	-	-	1.4
Distillation: 5 Wt%	-	358°F	480°F
(D-2887) 10	-	386	491
30	-	418	577
50	-	435	735
70	-	457	868
90	-	484	868 1008
95	-	490	-
RVP, psi	7.2	0	
Metals (ppm) Ni	-	-	4
Va	-	-	10
Na	-	-	3
Fe	-	-	16
Viscosity, cp at 140°F	-	1.19	-
210°F	-	0.79	6.19
Bromine No.	-	7.2	-
MAV	-	2.8	-
Ramsbottom Carbon, Wt%	-	-	3.01
Phenols (g.c.), ppm	-	30	-

\*Due to volatile nature, unable to obtain accurate results.

## 5. Commercial Yield Projections

Data from sections 1-4 were evaluated and correlated to commercial plant operations as shown in Table 28. Each of these feedstocks, with the possible exception of the Sunnyside material, should respond well to ART treating. Uncertainties are highest for the Sunnyside and the Westken materials due to the dilution encountered and/or required.

## Conclusions - Art Processing

Art Processing conclusions include:

- DILUENTS

- Diluents are required for the Westken crude, but San Ardo and Hondo can be processed as-received.
- Diluent boiling range does not have a major yield impact within the 400-700°F range.
- Hydrotreating the diluent reduces gas yields and conversion while possibly increasing coke yield.
- Increasing diluent quantity increases total conversion and coke yields.

- SEPARATIONS

- Atmospheric and/or vacuum fractionation prior to ART treating does not appear warranted, at least for the Westken Crude.
- Solvent deasphalting does not appear advantageous prior to ART treating.

Table 28  
Summary ART Yields at Estimated  
Optimum Operation

All Units Wt% of Feed

	<u>Westken</u>	<u>Hondo</u>	<u>San Ardo</u>	<u>Sunnyside</u>
H <sub>2</sub> S	0.2	0.9	0.3	0.0
Dry Gas	2.6	2.0	1.6	1.9
Wet Gas	2.1	3.0	1.7	5.6
C <sub>5</sub> - 430°F	7.4	23.2	9.0	22.5
430 - 630°F	23.2	19.7	22.4	60.9
630°F+	52.9	42.4	56.6	4.1
Coke	11.0	8.8	8.4	5.0
Conversion	24	28	22	25

- SPECIFIC ART RESPONSES

- All stocks respond favorably to demetallization.
- High naphtha yields are observed for the Hondo stock, primarily due to virgin naphtha content.
- Good asphaltene removal was observed, but metals removal was slightly less than anticipated.
- Demetallation is not required for the as-received (diluted) Sunnyside material.

CRACKING (RCC)

Tar sand bitumen and heavy oils are predominantly higher boiling materials than conventional petroleum. Additionally, contaminants such as metals and carbon residue not removed in the demetallization step, plus high levels of poisons such as basic nitrogen, are common. RCC conversion provides good control over these factors, while providing efficient boiling range conversion without sensitivity to particulates, water, and then negative items in the feed.

Figure 13 portrays a commercial RCC system. The demetallized and/or raw feedstock is contacted at the base of the riser with a qualified RCC catalyst. Oil, catalyst, and product vapors are transported in dilute phase up the riser, to the point where products and catalyst are rapidly disengaged to control overcracking. The spent catalyst



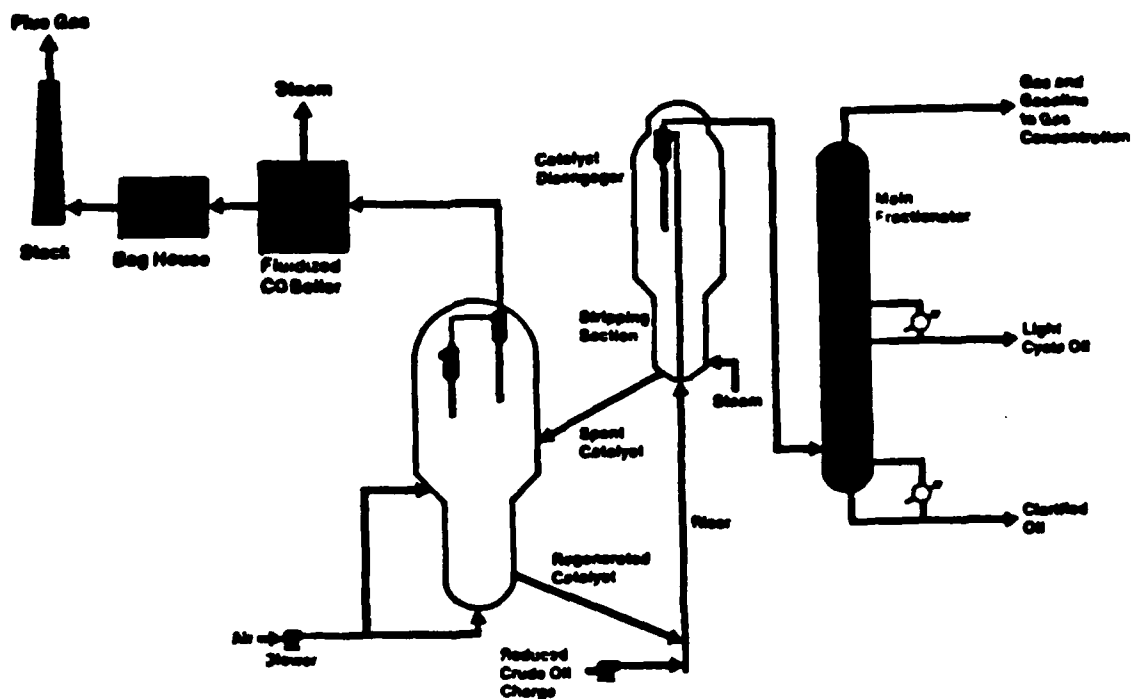


Figure 13. Process Flow Diagram--Commercial RCC Unit

Reference: Busch, et.al., 1984 NPRA Meeting (3/25-27/84)

returns to the regenerator, where the deposited carbon is burned off in a special two-stage regeneration. The hot, regenerated catalyst is then returned to the riser for reuse. Gaseous and liquid products from the riser are separated in a conventional main column and gas concentration plant. Regenerator off gases are routed through fluidized limestone boilers to recover remaining heat values and to reduce SO<sub>x</sub> emissions.

Key elements of the RCC process are the recirculating, continuously regenerated catalyst, strict catalyst/oil contacting control, rapid spent catalyst disengaging, controlled carbon removal, multi-stage regeneration, improved catalyst composition, and sophisticated metals management techniques. These aspects allow the capability to process heavy, contaminated crudes, the capability to accumulate one weight percent metals on catalyst (or more), selective production of transportation fuels and, in particular, direct production of high octane gasoline. RCC technology allows maximum utilization of the natural hydrogen content of a feedstock.

Phase I defined the following elements for experimentation during this portion of the program:

- Catalyst selection
- Effect of donors/diluents
- Process severity

Requirements for pretreatment were defined by the material properties; pretreatment was judged not required for the low metals content Sunnyside blend.

#### Catalyst Selection

Three qualified RCC-class catalysts were tested in a laboratory, fixed-fluidized bed using demetallized 500°F+ Westken feedstock. These catalysts were commercial equilibrium catalysts of similar history, with MAT activities (conversion) in the range of 65-70 volume percent. In addition to composition, catalyst metals content differed, ranging from a low of 4000 ppm nickel plus vanadium for sample 3 to a high of 7200 ppm nickel plus vanadium for sample 1.

Results of these tests are summarized in Table 29. Yields from each are remarkably similar; the primary difference is coke yield. These trends are also consistent with prior experience for these catalysts on ART treated petroleum feeds. Based on these data, catalyst #2, with lowest coke production, was selected for further testing.

#### Donor Effects

Very hydrogen deficient stocks may be better suited to hydroprocessing than RCC treatment, since at least threshold levels of hydrogen are required for adequate conversion and light yield production. Three tests were performed to

Table 29  
Comparison of Yields of Varying RCC<sup>sm</sup> Catalysts Using  
500°F+ Demetallized Westken

	All Units Wt% of Feed		
	4000 Ni 1	Catalyst 2	7200 Ni 3
Dry Gas	1.6	1.7	1.5
Wet Gas	4.8	6.1	4.8
C <sub>5</sub> - 430°F	22.4	23.8	24.6
430 - 630°F	42.2	42.2	42.4
630F+	19.6	19.2	18.4
Coke	9.5	7.1	8.3
430°F Conversion	38.3	38.6	39.3
C <sub>5</sub> - 430°F Selectivity	58.4	61.5	62.8

evaluate this impact on the low hydrogen content Westken feedstock, using the laboratory fixed fluidized bed. The donor for this evaluation was the hydrotreated cycle oil described earlier.

Results are shown in Table 30. Small impacts on dry gas and wet gas were noted, with some distributional differences between gasoline and distillate. The remarkable effect, however, is the indicated reduction in coke and increase in 630°F+ conversion. As a result, use of donor diluent (where available) will be recommended for very refractory, hydrogen-deficient stocks.

#### Feedstock/Process Severity

Process severity requirements are a function of feedstock, so yield curves were developed for each feedstock on continuous pilot units. Products were collected from these tests, composited, fractionated, and analyzed. Remaining products were used to produce samples for further processing.

##### 1. Westken

Demetallized Westken 500°F+ product from ART treating (Table 20) was used for feedstock in this study. About 50 percent of this product represented LCO diluent surviving the ART processing, and as a result, the process response measured must be qualified on this basis. The diluent used is very refractory without hydroprocessing and results in suppressed

Table 30

Estimation of RCC Donor Effect Using Blends of  
500°F+ Westken Demetallized Oil and Hydrotreated Donor

All Units Wt%

	<u>Donor Alone</u>	<u>50% Donor 50% Oil</u>	<u>Calculated Oil</u>	<u>Observed Oil</u>
Dry Gas	0.7	1.2	1.8	1.5
Wet Gas	6.8	6.4	5.9	4.8
C <sub>5</sub> - 430°F	51.6	35.1	18.5	24.6
430 - 630°F	35.2	44.1	52.9	42.4
630°F+	3.5	9.2	15.0	18.4
Coke	2.2	4.0	5.9	8.3
430°F Conversion	53.1	41.6	32.0	39.3
430°F Selectivity	64.3	63.3	57.8	62.8

RCC conversion and product yields. Nevertheless, results are directionally consistent, particularly on a feedstock quality basis.

Three material balances were performed with 430°F+ conversions ranging from 36-42 weight percent. Table 31 presents these data, while Figure 14 presents the smoothed yield curves. The overbearing influences of the petroleum LCO, plus low hydrogen content of the feedstock, result in low conversion and transportation fuel yields. As a result, this feed is recommended for use with a hydrotreated recycle diluent, both for diluent impact plus increased mid-distillate conversion.

Products from this test were composited and fractionated into the cuts shown in Table 32. The gasoline cuts are much higher in octane and aromatics than normally observed with moderate sulfur and nitrogen. The heavier components are very hydrogen deficient, measuring essentially all aromatics.

## 2. Hondo

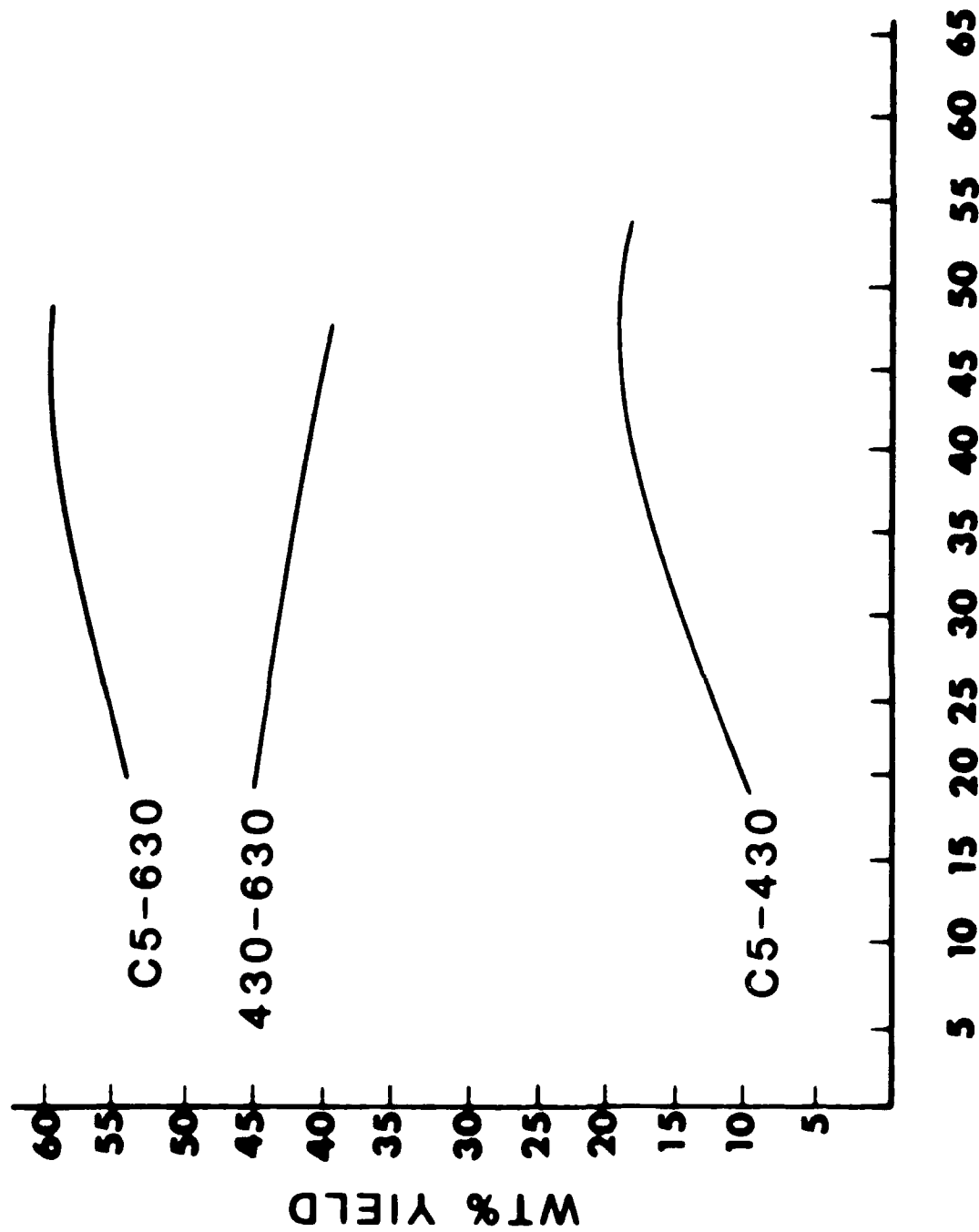
Demetallized Hondo 500°F+ product from ART treating was used for this study; properties of this feedstock were shown in Table 22. Five material balances were performed at conversions ranging from 45-46% wt., Table 33. These results translate into the smoothed curves shown in Figure 15,

Table 31

RCC Response for Demetallized 500°F+ Westken

Run No.	B1435-030	B1435-032	B1435-033
H <sub>2</sub> , SCF/BBL	217	117	215
LCO/HCO Wt. ratio	2.08	1.79	2.34
Conversion, Vol. %	40.14	38.88	44.47
Selectivity (Gasoline)	0.61	0.57	0.61
Component Yields	Wt. %	Wt. %	Wt. %
H <sub>2</sub>	0.33	0.18	0.32
C <sub>1</sub>	1.13	1.21	1.40
C <sub>2</sub> 's	1.82	1.53	1.63
C <sub>3</sub>	0.43	0.36	0.41
C <sub>3</sub> =	2.77	2.19	2.98
IC <sub>4</sub>	0.58	0.49	0.7
NC <sub>4</sub>	0.12	0.13	0.17
B <sub>1</sub> + IC <sub>4</sub> =	1.47	1.49	1.76
TB <sub>2</sub>	0.55	0.57	0.71
CH <sub>2</sub>	0.26	0.42	0.56
C <sub>5</sub> -430°F	19.48	17.82	21.35
430°-630°F	42.12	40.82	40.48
630°F+	20.2	22.81	17.33
Coke	8.46	9.78	9.93





CONVERSION

DEMETALLIZED WESTKEN RCC YIELDS

FIGURE 1

TABLE 32  
Properties of Hestken RCC Products

	C <sub>5</sub> -330	330-430	430-520	520-600	600+°F
Yield, Wt%	16.04	6.18	12.80	25.43	39.55
API	54.4	28.9	14.7	13.1	0.2
H <sub>2</sub> Wt%	12.22	10.40	8.84	8.98	7.53
N <sub>2</sub> Total ppm (or Wt%)	36ppm	179ppm	243ppm	234ppm	(.18%)
N <sub>2</sub> Basic ppm (or Wt%)	14ppm	0.02%	55ppm	14ppm	90ppm
Sulfur Wt%	135ppm	0.25%	1.57%	1.32%	2.54%
FIA					
Saturates Vol%	11.8	4.3	5.6	0.0	-
Olefins	61.2	11.8	1.1	0.4	-
Aromatics	27.0	83.9	93.3	99.6	-
HPLC					
Saturates Vol%	-	-	-	-	9.1
Mono Aromatics	-	-	-	-	1.0
Di Aromatics	-	-	-	-	16.2
Tri Aromatics	-	-	-	-	62.6
Polars	-	-	-	-	8.4
Asphaltenes	-	-	-	-	2.6
Distillation: 5 Wt%	90	319	430	483	578
10	107	327	444	490	598
30	179	351	453	522	619
50	234	375	476	539	670
70	279	397	488	556	714
90	311	414	506	585	888
95	325	429	517	598	996
RVP, psi	10.7	0	-	-	-
Viscosity at 140°F			1.38	2.01	14.1
210°F			1.95 (100°)	3.15 (100°)	4.2
Phenols (g.c.) ppm	50	70	-	-	-
Blended Octane	98.2	100.2	-	-	-

Table 33

Demetallized 500°F. Mondo RC Response

Run No.	B1372-186	B1372-188	B1372-190	B1372-184	B1372-195
H <sub>2</sub> , SCF BBL	149	228	258	146	196
Eff. H <sub>2</sub> Wt. Ratio	1.11	1.22	1.32	1.26	1.29
Conversion, %	45.6	51.8	56.9	56.9	57.4
Solubility Coefficient	0.76	0.82	0.64	0.66	0.71
Component Fields	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %
H <sub>2</sub>	0.22	0.35	0.39	0.22	0.30
C <sub>1</sub>	0.91	1.18	1.68	1.11	1.04
C <sub>2</sub> 's	1.30	1.73	1.87	2.0	1.64
C <sub>3</sub>	0.40	0.51	0.52	0.64	0.50
C <sub>4</sub>	1.54	2.31	2.56	3.55	2.61
C <sub>4</sub> +	0.19	0.28	0.35	0.66	0.44
N <sub>2</sub>	0.60	0.16	0.18	0.27	0.16
H <sub>2</sub> + C <sub>4</sub> +	0.99	1.70	2.15	2.76	2.15
TH <sub>2</sub>	0.42	0.61	0.82	1.1	0.84
CH <sub>2</sub>	0.31	0.48	0.71	0.83	0.75
CH <sub>3</sub> -430°F	27.50	25.52	28.94	29.69	32.08
430°F to 500°F	29.77	27.35	25.14	24.8	24.82
500°F+	6.64	22.47	19.19	19.65	19.24
Total	88.05	13.53	13.49	10.49	11.66

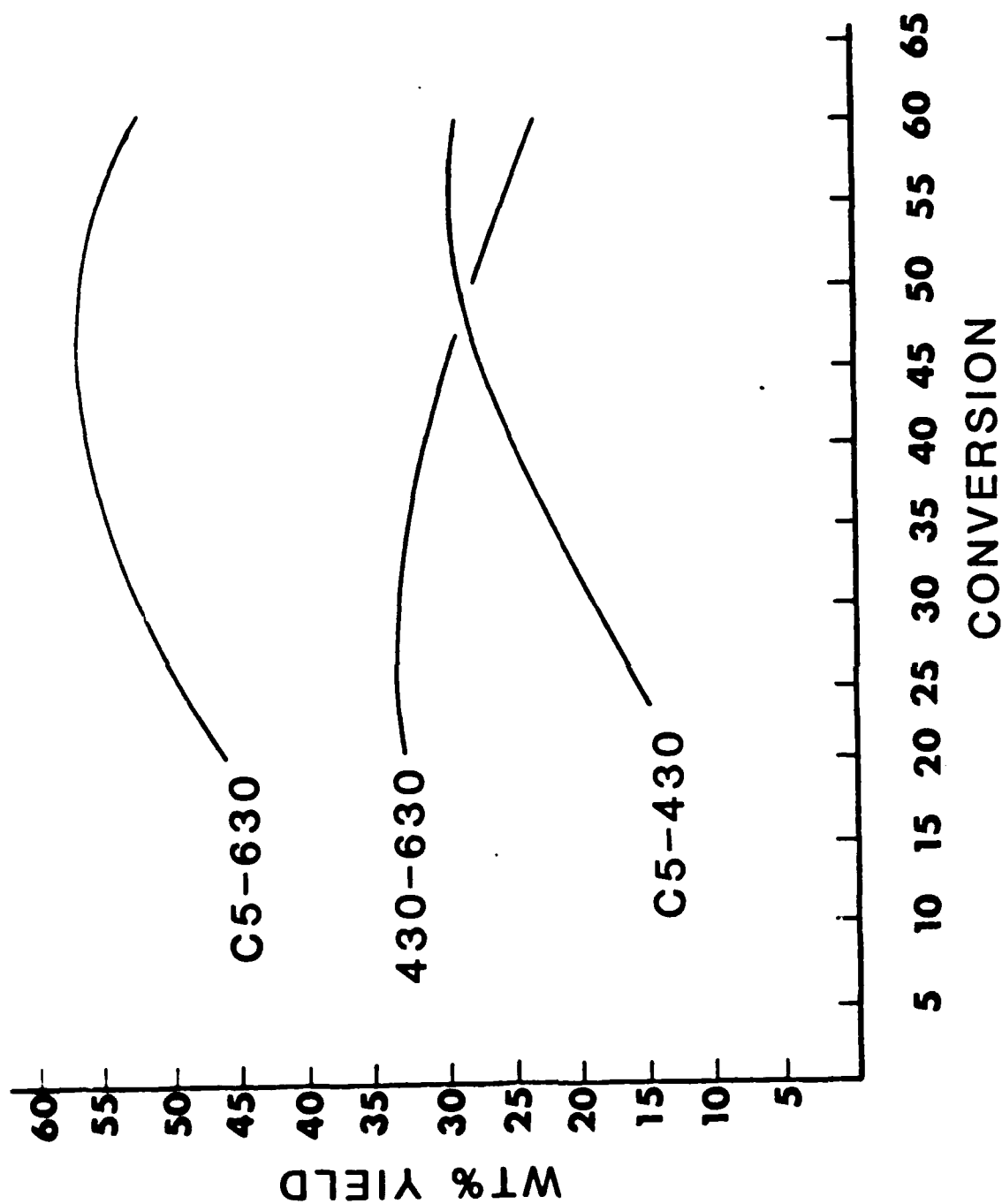


FIGURE 15

## DEMETALLIZED HONDO RCC

showing maximum transportation fuel yields at about 45-50 wt.% conversion.

Products from these tests were composited and fractionated as shown in Table 34. The gasoline showed excellent octanes, with lower nitrogen and slightly more hydrogen content than the Westken product; this material cannot be used directly due to 0.1% sulfur specification maximums. Heavier products were aromatic, and had higher hydrogen content than the Westken products. Sulfur removal by hydrotreatment would be required prior to use of these materials as fuels.

### 3. San Ardo

Demetallized 500°F+ San Ardo, surprisingly, was probably the easiest demetallized stock to crack. Properties of the feed (Table 24) were similar to the Hondo, with slightly less hydrogen and more nitrogen, and significantly less sulfur. Component analysis of the feed showed slightly more saturates in the San Ardo material.

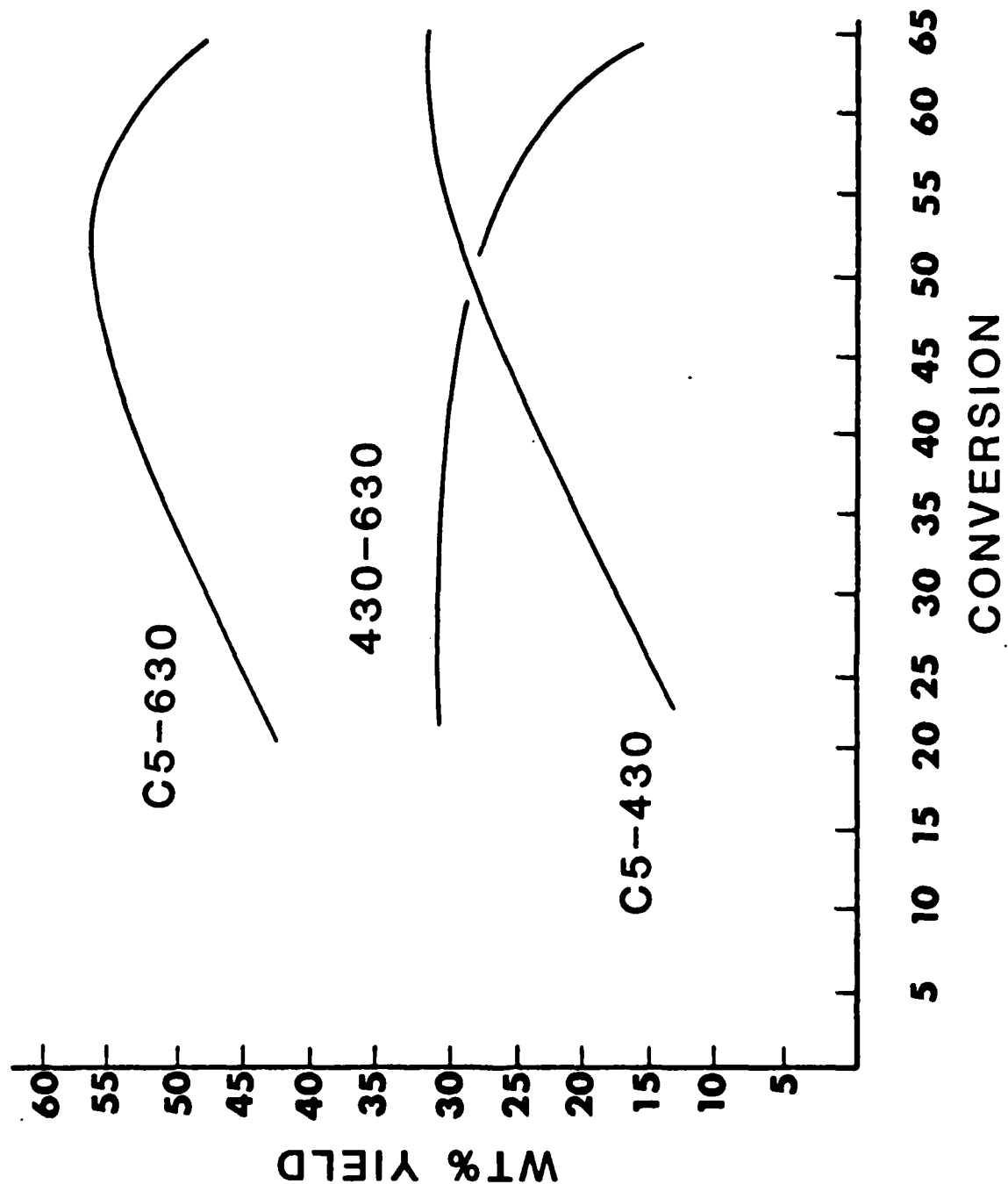
Four material balances were performed on the San Ardo with conversions ranging from 44-64 wt.%, Table 35. The gasoline base was not attained, but a maximum C<sub>5</sub>-630°F yield was noted at about 55 wt% conversion, Figure 16.

Table 34  
Composite Product Properties from RCC Processing of  
Demetallized Hondo Oil

	C5-330	330-430	430-520	520-600	600+°F
Yield, Wt%	19.20	8.11	9.67	14.85	48.17
API	57.0	33.0	23.9	21.6	4.6
H <sub>2</sub> Wt%	12.57	11.27	10.53	10.53	8.57
N <sub>2</sub> Total ppm(or Wt%)	124	368	(0.13%)	(0.17%)	(0.70%)
N <sub>2</sub> Basic ppm(or Wt%)	126	(.03%)	(.02%)	(.04%)	(0.06%)
Sulfur Wt%	1.57	2.57	3.68	4.04	4.52
FIA					
Saturates Vol%	9.7	6.9	17.4	22.9	-
Olefins	70.8	31.1	14.2	0.0	-
Aromatics	19.5	62.0	68.4	77.1	-
HPLC, Wt%					
Saturates Vol%	-	-	-	-	17.3
Mono Aromatics	-	-	-	-	4.3
Di Aromatics	-	-	-	-	12.7
Tri Aromatics	-	-	-	-	48.4
Polars	-	-	-	-	12.4
Asphaltenes	-	-	-	-	4.9
Distillation: 5 Wt%	90°F	320°F	394°F	433°F	580°F
10	104	329	413	459	611
30	173	355	453	512	666
50	227	377	478	537	724
70	266	399	492	564	811
90	302	423	512	594	975
95	322	436	520	607	1015 at 93%
RVP, psi	7.3	0			
Viscosity in cp at 140°F			1.37	2.02	-
210°F			0.88	1.19	7.72
Phenols (g.c.) ppm	130	75	-	-	-
Blended Octane	105	97	-	-	-

Table 35

RCC Response For Demetallized 500°F+ San Ardo				
Run No.	B1435-004	B1372-199	B1372-197	B1435-002
H <sub>2</sub> , SCF/BBL	156	173	178	192
LCO/HCO Wt. Ratio	1.08	1.1	1.08	1.62
Conversion, Vol. %	45.04	46.32	49.56	65.19
Selectivity (Gasoline)	0.70	0.67	0.68	0.63
Component Yields	Wt. %	Wt. %	Wt. %	Wt. %
H <sub>2</sub>	0.24	0.26	0.27	0.29
C <sub>1</sub>	0.78	1.11	1.07	1.98
C <sub>2</sub> 's	1.04	1.28	1.38	1.90
C <sub>3</sub>	0.33	0.4	0.42	0.55
C <sub>3</sub> =	1.76	1.96	1.9	3.72
IC <sub>4</sub>	0.32	0.34	0.30	0.80
NC <sub>4</sub>	0.13	0.12	0.14	0.24
B <sub>1</sub> + IC <sub>4</sub> =	1.53	1.89	1.79	2.91
TB <sub>2</sub>	0.48	0.62	0.59	1.14
CB <sub>2</sub>	0.37	0.48	0.49	0.91
C <sub>5</sub> -430°F	25.02	24.68	26.76	31.97
430°-630°F	29.31	29.13	27.17	22.10
630°F+	27.09	26.56	25.16	13.62
Coke	11.04	10.61	12.12	17.32



# DEMETALLIZED SAN ARDO RCC

FIGURE 16



Fractionated products, Table 36, demonstrated the highest gasoline octane of any of the feedstocks processed. Most fractions were similar to the Hondo products except for sulfur and nitrogen contents.

#### 4. Sunnyside

Because of the highly dilute nature of the Sunnyside stock, and inconsistent results when separation of the diluent was attempted, RCC processing of the as-received stock was provided. Table 5 presents properties of this feed.

Six cracking tests were performed on this feed. All tests except for the first had low weight recoveries; tests of other feeds, before and after this series, were acceptable. This may indicate coke deposition at some point in the system not normally measured.

Tables 37 and 38 summarize these test results, plus two tests on a comparable kerosene diluent. Attempts were made to mathematically remove the kerosene yields, with limited success; C<sub>5</sub>-630 yields for Sunnyside without diluent appeared to be 50-60 wt%. As-received results are shown in Figure 17, compared with the other feeds. These data should be used with caution.

Sunnyside product properties, Table 39, reflect the presence of the kerosene diluent. The low 330-430°F octane is

Table 36

## Composite Properties for San Ardo RCC Products

	C <sub>5</sub> -330	330-430	430-520	520-600	600+°F
Yield, Wt%	24.57	7.70	10.10	19.40	38.23
API	51.6	31.5	23.1	20.6	6.2
H <sub>2</sub> Wt%	12.41	10.94	10.58	10.69	8.84
N <sub>2</sub> Total ppm(or Wt%)	213	835	(0.20%)	(0.26%)	(0.83%)
N <sub>2</sub> Basic ppm(or Wt%)	81	(0.047%)	(.0318%)	(.0338%)	(0.0744%)
Sulfur Wt%	0.6%	0.91%	1.12%	1.35%	1.36%
PIA					
Saturates Vol%	8.3	3.2	6.4	0.0	-
Olefins	59.6	25.2	12.0	2.6	-
Aromatics	32.1	71.6	81.6	97.4	-
HPLC, Wt%					
Saturates Vol%	-	-	-	-	20.4
Mono Aromatics	-	-	-	-	4.3
Di Aromatics	-	-	-	-	11.9
Tri Aromatics	-	-	-	-	45.3
Polars	-	-	-	-	14.0
Asphaltenes	-	-	-	-	4.1
Distillation: 5 Wt%	98°F	284°F	393°F	441°F	592°F
D (2887) 10	109	311	407	475	612
30	191	344	446	515	663
50	237	374	469	538	722
70	284	397	491	563	805
90	331	424	522	593	962
95	354	440	536	606	1007 at 93%
RVP, psi	5.7	0	-	-	-
Viscosity at 140°F		0.84	1.40	2.21	-
210°F			0.92	1.23	9.10
Phenols (g.c.) ppm	200	210	-	-	-
Blended Octane	108	107	-	-	-

Table 37

RCC YIELD SUMMARY TABLE FOR  
AS-RECEIVED SUNNYSIDE TAR SANDS \*

Test No.	R1359-	072	074	079	081	085	088
Operating Conditions							
Feed Rate lbs/hr		9.15	5.4	7.2	7.4	7.0	11.0
Riser Temp °F		950	950	952	975	975	912
Cat/Oil Wt Ratio		8.9	9.0	9.5	8.0	12.5	6.3
Conversion, Vol%		75.4	79.1	81.97	78.7	81.98	71.95
H <sub>2</sub> O (Wt% of Feed)		13	19	7	9	9	5
Wt Recovery, Wt%		97.7	86.5	82.5	91.8	82.2	93.4
Wt% Component Yields							
Methane		0.55	0.82	1.13	0.87	1.16	0.52
Ethane & Ethylene		1.08	1.28	1.40	1.22	1.58	0.42
Propane		0.94	0.97	1.20	0.86	1.18	0.87
Propylene		5.15	6.45	6.99	5.31	7.46	3.94
C <sub>4</sub> Saturates		3.46	3.58	4.65	3.12	4.27	3.38
C <sub>4</sub> Olefins		5.83	6.92	7.50	6.11	8.07	4.71
C <sub>5</sub> -430°F		50.80	50.89	46.88	47.68	47.38	50.80
430°F+		26.17	22.22	19.16	22.63	19.15	29.82
430-630		25.83	20.99	18.23	21.82	18.57	29.04
630°F+		0.34	1.23	0.93	0.81	0.58	0.78
Coke		5.92	6.74	10.91	12.09	9.59	5.44
H <sub>2</sub> Scf/bbl		57	66	87	62	85	56

\* Feed contains 70% Kerosene Diluent

Table 38

RCC YIELD SUMMARY TABLE FOR  
SUNNYSIDE KEROSENE DILUENT ONLY

Test No.	R1359-	60	61
Operating Conditions			
Feed Rate lbs/hr		9.9	11.8
Riser Temp °F		950	921
Cat/Oil Wt Ratio		2.8	4.7
Conversion, Vol%		83.6	82.5
H <sub>2</sub> O (Wt% of Feed)		13	10
Wt Recovery, Wt%		95.2	96.0
Wt% Component Yields			
Methane		0.36	0.26
Ethane & Ethylene		0.66	0.50
Propane		0.77	0.78
Propylene		4.52	3.87
C <sub>4</sub> Saturates		3.69	4.16
C <sub>4</sub> Olefins		6.49	5.17
C <sub>5</sub> -430°F		62.28	64.43
430°F+		17.13	18.18
430-630		15.84	17.81
630°F+		1.29	0.86
Coke		4.04	2.01
H <sub>2</sub> Scf/bbl		22	23

Table 39

Composite Product Properties from RCC Processing  
of As-Received Sunnyside Oil

	C <sub>5</sub> -330	330-430	430-520	520-600	600+°F
Yield, Wt%	40.71	23.49	32.13	2.27	1.39
API	63.9	44.0	41.8	13.6	0
H <sub>2</sub> Wt%	12.97	12.79	13.37	9.20	7.00
N <sub>2</sub> Total ppm(or Wt%)	14	21	9	254	(0.16%)
N <sub>2</sub> Basic ppm(or Wt%)					
Sulfur ppm (or Wt%)	154	176	335	(.23%)	(.77%)
FIA					
Saturates Vol%	27.7	58.2	84.9	-	-
Olefins Vol%	49.0	2.4	1.8	1.4	-
Aromatics	23.3	39.4	13.3	98.6	-
HPLC, Wt%					9.9
Saturates Vol%					1.7
Mono Aromatics	-	-	-	-	22.2
Di Aromatics	-	-	-	-	43.9
Tri Aromatics	-	-	-	-	9.0
Polars	-	-	-	-	13.4
Asphaltenes	-	-	-	-	
Distillation: 5 Wt%	5°F	323°F	416°F	498°F	628°F
D (2887) 10	62	334	422	515	638
30	124	377	446	528	674
50	171	395	462	538	710
70	233	411	472	555	763
90	285	429	494	584	868
95	301	438	499	601	919
RVP, psi	12.70	0			
Viscosity in cp at 140°F		0.91	1.28	2.24	-
210°F					12.58
Phenols (g.c.) ppm	60	17			
Blended Octane	96.8	44.6	-	-	-

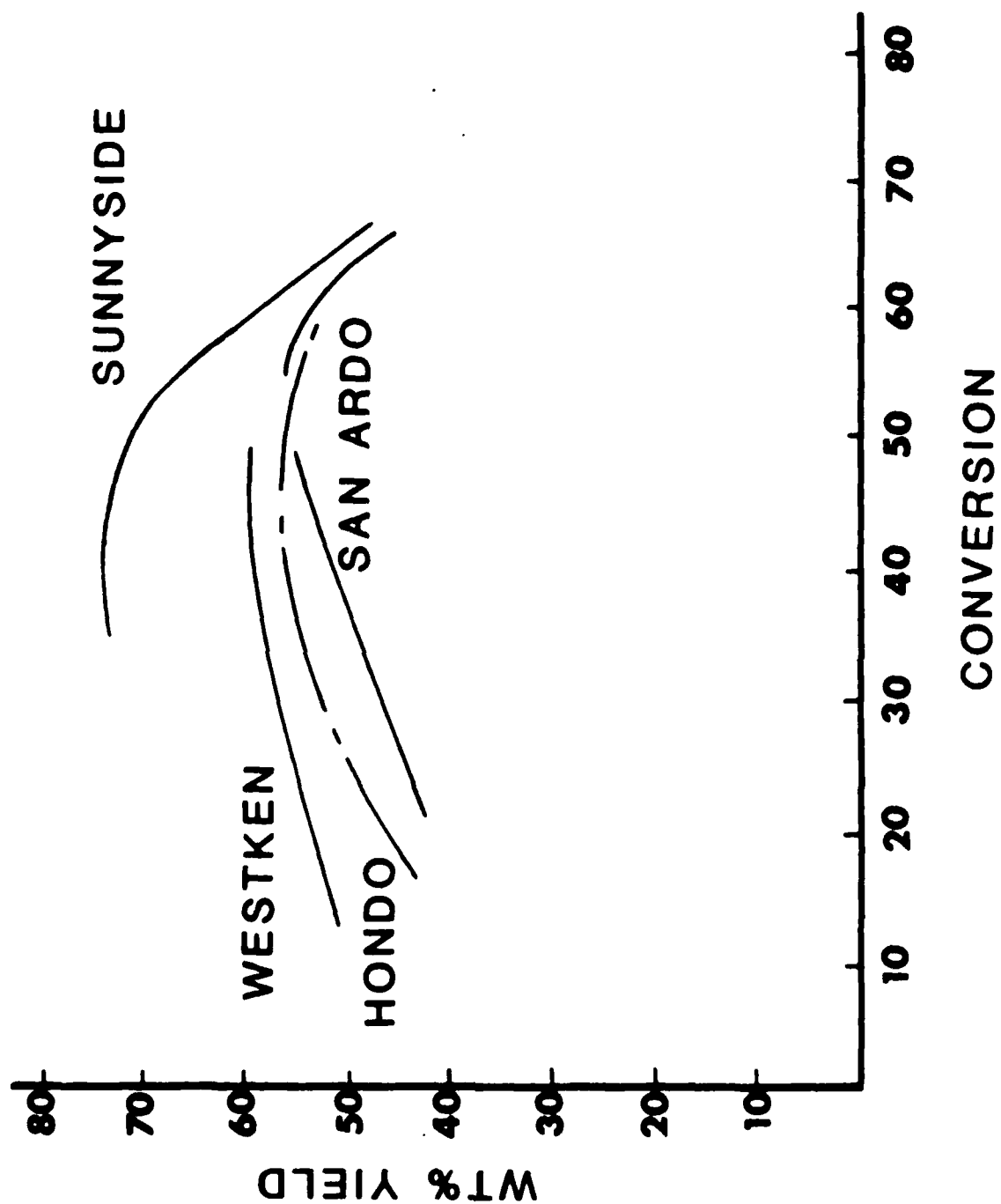


FIGURE 17  
TOTAL TRANSPORTATION FUELS

probably due to unconverted kerosene product. Sunnyside products, contrasted to those assumed from the paraffinic kerosene, are heavily multi-ring aromatic.

### Conclusions

These data result in the following conclusions:

- Catalyst selection is consistent with petroleum experience; present commercial RCC catalysts are applicable.
- Hydrogen donors can positively impact performance, primarily by reducing coke yield when processing highly aromatic stocks.
- Transportation fuel production of 55-60 wt% is attained at relatively low conversion (40-60 wt%).
- Hydrogenation of a heavy recycle stream will be required for (1) sulfur removal, (2) increased total conversion, and (3) donor capability.

### HYDROTREATING JP-8 AND JP-4 PRECURSORS

Production of turbine fuels from RCC syncrudes requires relatively high hydrogen inputs to saturate olefinic and aromatic compounds, and lower sulfur and nitrogen compounds to acceptable levels. ART and RCC product distillate fractions from four heavy oils/bitumens (Hondo, San Ardo, Westken, and Sunnyside) were each blended appropriately to make JP-4 and JP-8 precursors, followed by hydrotreatment at severities providing the necessary hydrogen input.

### Feedstock Sources and Blends

The flow scheme in Figure 18 shows the various ART and RCC fractions used in the hydrotreater feed blends. Table 40 lists the composition of the eight feed blends. The material balance yields of the MRS and RCC steps were considered together so that total feed to the hydrotreater was 100%.

### Equipment and Procedure

The equipment used for hydrotreating the turbine fuel precursors is shown in Figure 19. The reactor was a 1" I.D. x 49" long stainless steel vessel. Liquid was charged downflow to the reactor by a Lapp diaphragm metering pump and hydrogen flow controlled with a Brooks mass flow meter and control valve. Four controllers adjust electrical heating of the four reactor zones. A small heat exchanger cools the product effluent and a Grove backpressure regulator controls system pressure while letting down product to atmospheric pressure. Product flows through a liquid collection system followed by gas separation, a cold trap and gas sample bombs. A wet scrubber and wet test gas meter are used just prior to the gases' being vented to the atmosphere.

The catalyst used in hydrotreating the turbine fuel precursors was a commercially available nickel molybdate catalyst of good denitrogenation and aromatic saturation activity. The catalyst was loaded into the reactor and void filled with Ottawa sand. Tabular alumina was used in the



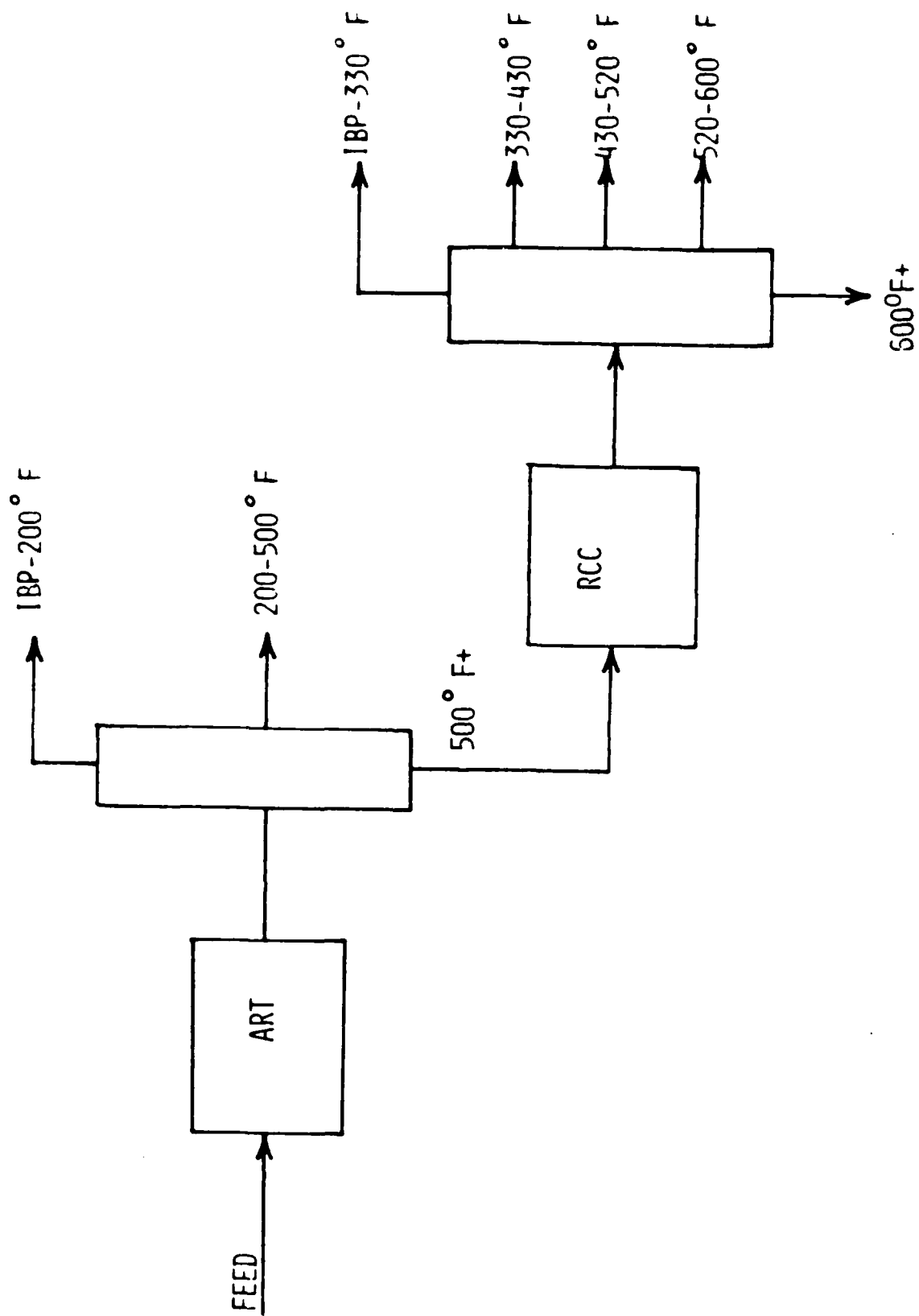


FIGURE 18. SCHEMATIC FLOW DIAGRAM FOR THE ORIGIN OF TURBINE FUEL PRECURSORS

TABLE 40

## TURBINE FUEL BLENDS FOR HYDROTREATING FEEDSTOCKS

JP-8 PRECURSORS

COMPONENT	SUNNYSIDE	SAN ARDO	HONDO	WESTKEN
ART 200-500°	—	48.9	55.1	28.8
RCC 330-430°	40.6	10.6	11.1	9.9
RCC 430-520°	55.5	13.9	13.3	20.5
RCC 520-600°	3.9	26.6	20.5	40.8

JP-4 PRECURSORS

COMPONENT	SUNNYSIDE	SAN ARDO	HONDO	WESTKEN
ART IBP-200°	—	9.5	25.8	8.7
200-500°	—	41.4	38.6	32.1
RCC IBP-330°	42.3	28.5	18.5	11.1
RCC 330-430°	24.4	8.9	7.8	4.4
RCC 430-520°	33.3	11.7	4.7	1.1

ALL WEIGHT PERCENT

AD-A185 744

AVIATION TURBINE FUELS FROM TAR SANDS BITUMEN AND HEAVY 2/2

OILS PART 2 LABOR. (U) ASHLAND PETROLEUM CO KY

H F MOORE ET AL. JUL 87 AFWAL-TR-84-2078-PT-2

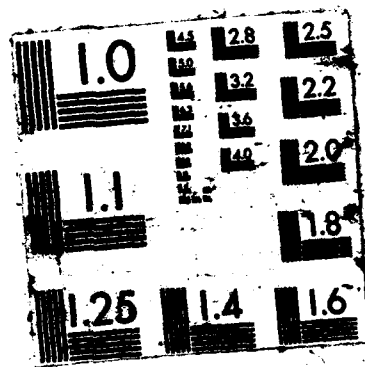
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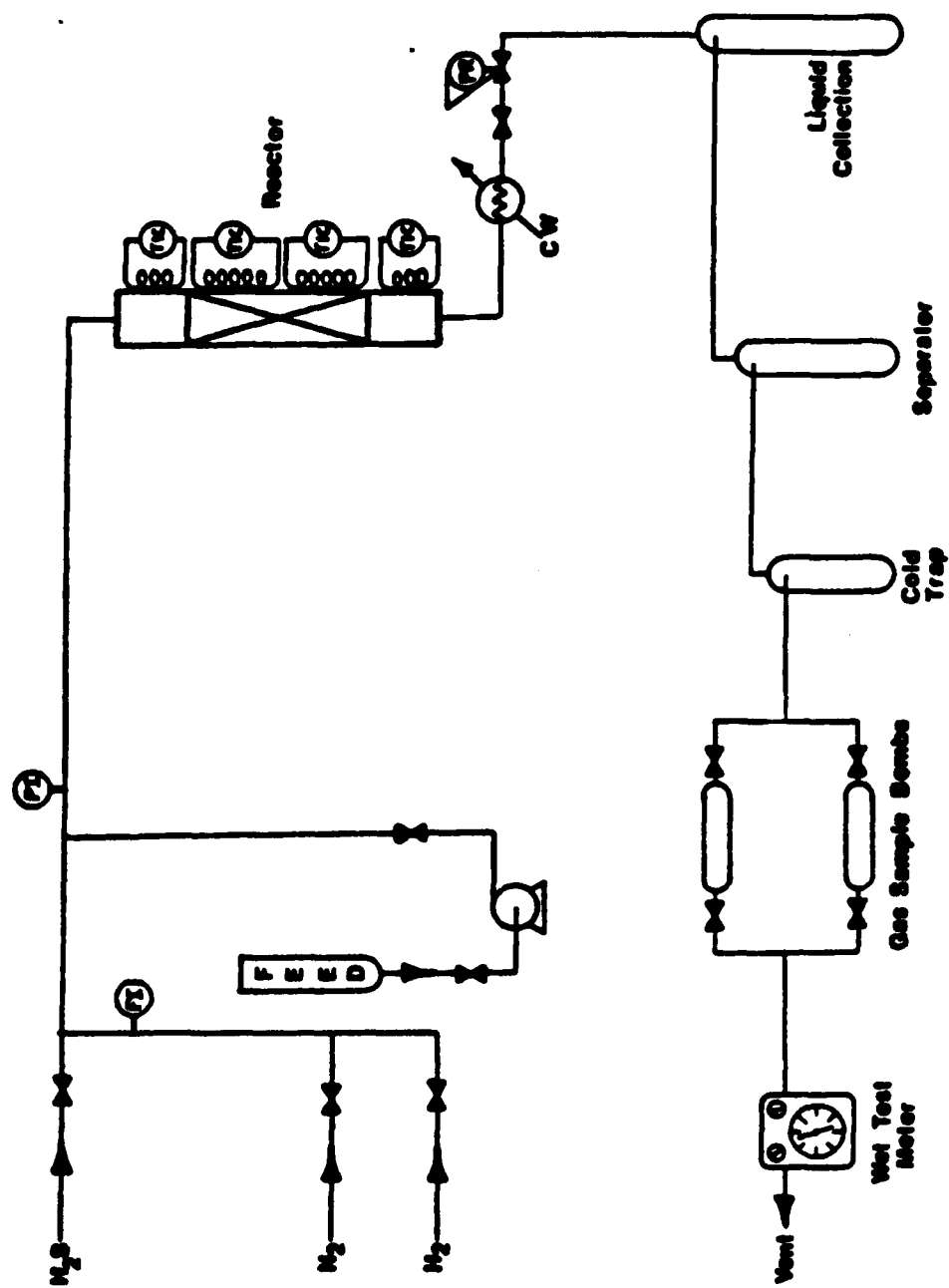


FIGURE 19. TURBINE FUEL HYDROTREATER

preheat and post heat sections. The catalyst was presulfided with hydrogen sulfide to 50°F above reaction temperature prior to startup.

The JP-8 precursor blends were used in the first two material balances of each run; the JP-4 precursors were used in the third and fourth material balances of each run. Run 139R was the exception with only one material balance. Products of each material balance were stripped of dissolved H<sub>2</sub>S on a one-inch diameter Todd column, then clay treated. Products that were suspected of still having dissolved H<sub>2</sub>S were either caustic and water-washed or collected over caustic pellets when redistilled to adjust final boiling point.

## Results

As-run material balances and actual test conditions are shown in Tables 41 through 45. All feed and product analyses are displayed in Tables 46 through 50.

Each hydrotreater feed was a blend of several streams. The processing history of the Sunnyside fuels differs from the others, however. Since the as-received Sunnyside was already highly diluted and relatively clean, it was routed directly to RCC processing, unlike the other three heavy oils and tar. Table 41, therefore, shows no ART IBP-200°F or 200-500°F components for Sunnyside feed blends to hydrotreating.

ART processing was performed on the San Ardo, and Hondo feedstocks as-received and on the Westken diluted 50 to 70% with RCC cycle oil. The resulting ART IBP -200°F and 200-500°F streams were stored and RCC processing was done on the 500°F+ fraction of the San Ardo, Hondo, and Westken ART products. Processing of each 500°F+ ART stream gave four different RCC distillate streams.

Blends of hydrotreater feedstock were then composited by material balance ratios from the appropriate ART and RCC fraction. The blended jet fuel precursors were hydrotreated to meet a variety of military specifications, as listed in Table 51. The major goals of the hydrotreating were to achieve acceptable aromatics content, °API gravity, and

TABLE 41

Hydrotreating Sunnyside Turbine Fuels - Run 138As - Run Balance

Feeds In:	<u>M.B. 1</u>	<u>M.B. 2</u>	<u>M.B. 3</u>	<u>M.B. 4</u>
Liquid Feed	100.00	100.00	100.00	100.00
Hydrogen	<u>4.77</u>	<u>4.94</u>	<u>5.09</u>	<u>5.16</u>
Total	104.77	104.94	105.09	105.16
Products: - In Wt% of Liquid Feed -				
Hydrogen	*4.05	3.95	4.33	3.80
C <sub>1</sub>	0.00	0.00	0.00	0.00
C <sub>2</sub>	0.01	0.46	0.01	0.10
C <sub>3</sub>	0.02	0.27	0.02	0.09
C <sub>4</sub>	0.18	0.10	0.19	0.33
C <sub>5</sub>	0.18	0.00	0.19	0.23
H <sub>2</sub> S	0.03	0.03	0.02	0.02
NH <sub>3</sub>	0.00	0.00	0.00	0.00
Liquids	<u>100.60</u>	<u>100.54</u>	<u>99.53</u>	<u>99.72</u>
Total	105.06	105.36	104.29	104.31
Closure, Wt%	100.28	100.40	99.24	99.19
Hydrogen Consumption SCFB	390	540	400	710
Temperature, °F	651	701	652	702
Pressure, psig	800	995	800	1003
LHSV, HR <sup>-1</sup>	2.20	1.06	2.13	1.05

\*Gas Analysis Estimated for M.B. 1 - Used M.B. 3 Analysis Due to Similar Conditions.



TABLE 42

Hydrotreating San Ardo Turbine Fuels - Run 139As - Run Balance

Feeds In:	<u>M.B. 1</u>	<u>M.B. 2</u>	<u>M.B. 3</u>	<u>M.B. 4</u>
Liquid Feed	100.00	100.00	100.00	100.00
Hydrogen	6.70	6.57	7.44	7.11
Total	106.70	106.57	107.44	107.11
Products: - In Wt% of Liquid Feed -				
Hydrogen	4.98	4.82	5.39	5.06
C <sub>1</sub>	0.00	0.21	0.00	0.21
C <sub>2</sub>	0.19	0.49	0.07	0.11
C <sub>3</sub>	0.20	0.02	0.12	0.15
C <sub>4</sub>	0.14	0.01	0.16	0.15
C <sub>5</sub>	0.05	0.00	0.18	0.06
H <sub>2</sub> S	1.11	1.11	0.92	0.92
NH <sub>3</sub>	0.10	0.10	0.06	0.06
Liquids	100.13	99.04	98.71	101.32
Total	106.91	105.82	105.60	108.03
Closure, Wt%	100.20	99.29	98.29	100.86
Hydrogen Consumption SCFB	1010	1020	1120	1120
Temperature, °F	686	711	675	701
Pressure, psig	1025	1210	1025	1215
LHSV, HR <sup>-1</sup>	1.03	0.78	0.99	0.77

TABLE 43

Hydrotreating Hondo Turbine Fuels - Run 140As - Run Balance

Feeds In:	<u>M.B. 1</u>	<u>M.B. 2</u>	<u>M.B. 3</u>	<u>M.B. 4</u>
Liquid Feed	100.00	100.00	100.00	100.00
Hydrogen	<u>7.24</u>	<u>7.30</u>	<u>8.14</u>	<u>7.80</u>
Total	107.24	107.30	108.14	107.80

## Products: - In Wt% of Liquid Feed -

Hydrogen	5.14	4.81	5.38	5.23
C <sub>1</sub>	0.00	0.00	0.00	0.12
C <sub>2</sub>	0.05	0.08	0.21	0.04
C <sub>3</sub>	0.06	0.08	0.45	0.07
C <sub>4</sub>	0.05	0.04	0.48	0.14
C <sub>5</sub>	0.04	0.00	0.14	0.33
H <sub>2</sub> S	3.29	3.26	2.70	2.69
NH <sub>3</sub>	0.06	0.06	0.04	0.04
Liquids	<u>100.99</u>	<u>98.35</u>	<u>98.66</u>	<u>99.83</u>
Total	109.67	106.69	108.06	108.49
Closure, Wt%	102.26	99.43	99.93	100.64
Hydrogen Consumption SCFB	1200	1420	1460	1360

Temperature, °F	674	701	659	686
Pressure, psig	1025	1215	1020	1220
LHSV, hr <sup>-1</sup>	1.01	0.75	0.97	0.76

TABLE 44

Hydrotreating Westken Turbine Fuels - Run 141As - Run Balance

Feeds In:	<u>M.B. 1</u>	<u>M.B. 2</u>	<u>M.B. 3</u>	<u>M.B. 4</u>
Liquid Feed	100.00	100.00	100.00	100.00
Hydrogen	<u>8.44</u>	<u>8.48</u>	<u>9.21</u>	<u>9.41</u>
Total	108.44	108.48	109.21	109.41
Products: - In Wt% of Liquid Feed -				
Hydrogen	3.56	3.72	5.55	6.22
C <sub>1</sub>	0.00	0.00	0.00	0.00
C <sub>2</sub>	0.23	0.17	0.08	0.31
C <sub>3</sub>	0.26	0.01	0.15	0.34
C <sub>4</sub>	0.14	0.01	0.08	0.33
C <sub>5</sub>	0.00	0.01	0.10	0.30
H <sub>2</sub> S	1.28	1.28	0.76	0.75
NH <sub>3</sub>	0.03	0.03	0.02	0.02
Liquids	<u>103.12</u>	<u>97.55</u>	<u>98.96</u>	<u>98.89</u>
Total	108.61	102.79	105.70	107.15
Closure, Wt%	100.16	94.76	96.78	97.94
Hydrogen Consumption SCFB	3040	2960	2080	1810
Temperature, °F	701	703	687	687
Pressure, psig	2020	1999	2010	2008
LHSV, HR <sup>-1</sup>	0.50	0.50	0.51	0.49

TABLE 45

Re-Hydrotreating San Ardo Turbine Fuel - Run 139RAs - Run Balance

Feeds In:	<u>M.B. 1</u>
Liquid Feed	100.00
Hydrogen	<u>7.26</u>
Total	107.26

## Products: - In Wt% of Liquid Feed -

Hydrogen	5.53
C <sub>1</sub>	0.08
C <sub>2</sub>	2.74
C <sub>3</sub>	4.07
C <sub>4</sub>	3.15
C <sub>5</sub>	0.54
H <sub>2</sub> S	0.00
NH <sub>3</sub>	0.00
Liquids	<u>98.62</u>
Total	114.73
Closure, Wt%	106.96
Hydrogen Consumption SCFE	970
Temperature, °F	707
Pressure, psig	1025
LHSV, HR <sup>-1</sup>	0.76

TABLE 46

## HYDROTREATER PRODUCT

RUN NO. 138

SUNNYSIDE

	<u>JP-8</u>			<u>JP-4</u>		
	<u>FEED</u>	<u>MB 1</u>	<u>MB 2</u>	<u>FEED</u>	<u>MB 3</u>	<u>MB 4</u>
API	41.4	44.0	46.8	48.3	50.6	53.8
H, WT.%	13.05	13.72	14.14	13.05	13.77	14.17
S, PPM (WT%)	301	20	19	214	13	6
N, PPM	18	1	1	15	1	1
RVP, PSIG	—	—	—	—	1.9	2.5
FIA : S		77.1	86.6		78.8	87.6
V O		1.0	1.0		0.3	0.8
L A		21.9	12.4		20.4	11.6
A						
SIM D, ° C						
IBP		130	89		-44	-36
10%		175	166		58	58
20%		196	193		92	91
50%		217	216		194	181
80%		247	245		238	236
FBP		328	307		266	263

TABLE 47

## HYDROTREATER PRODUCT

RUN NO. 139

SAN ARDO

	<u>JP-8</u>			<u>JP-4</u>		
	<u>FEED</u>	<u>MB 1</u>	<u>MB 2</u>	<u>FEED</u>	<u>MB 3</u>	<u>MB 4</u>
API	29.3	37.7	39.3	40.4	46.2	48.1
H, WT. %	11.53	12.82	13.04	11.84	13.34	13.66
S, PPM (WT %)	(1.05)	20	17	(0.87)	34	32
N, PPM	825	1	1	519	1	1
RVP, PSIG	—	—	—	—	2.6	2.0
FIA : S		65.5	71.5		79.6	87.8
VOL		0.8	1.1		0.8	0.8
LA		33.7	27.4		19.6	11.4
SIM D, °C						
IBP		78	62		-4	-39
10%		141	132		75	73
20%		168	161		107	100
50%		212	207		168	163
80%		272	266		237	234
FBP		329	327		284	280

TABLE 48

## HYDROTREATER PRODUCT.

RUN NO. 140

HONDO

	<u>JP-8</u>			<u>JP-4</u>		
	<u>FEED</u>	<u>MB 1</u>	<u>MB 2</u>	<u>FEED</u>	<u>MB 3</u>	<u>MB 4</u>
API	33.0	43.2	45.6	45.5	53.2	54.6
H, WT. %	11.75	13.37	13.71	12.47	14.09	14.34
S, PPM (WT %)	(3.1)	72	290	(2.54)	33	51
N, PPM	517	1	1	316	1	15
RVP, PSIG	—	—	—	—	2.9	2.8
FIA : S		71.4	82.8		87.2	93.3
V O		0.5	0.7		0.4	0.3
L A		28.1	16.5		12.4	6.4
λ						
SIM D, ° C						
IBP		62	67	18	5	
10%		134	118	68	67	
20%		157	144	91	91	
50%		199	191	144	143	
90%		267	255	227	225	
FBP		327	317	277	272	

TABLE 49

## HYDROTREATER PRODUCT

RUN NO. 141

WESTKEN

	<u>JP-8</u>			<u>JP-4</u>		
	<u>FEED</u>	<u>MB 1</u>	<u>MB 2</u>	<u>FEED</u>	<u>MB 3</u>	<u>MB 4</u>
API	19.2	37.9	38.2	33.7	53.2	54.6
H, WT. %	9.57	13.68	13.77	10.74	14.12	14.12
S, PPM (WT %)	(1.21)	21	31	(0.72)	53	113
N, PPM	227	1	1	160	1	1
RVP, PSIG	—	—	—	—	-2.5	
FIA : S	5.1	95.2	95.6	13.1	98.1	98.9
V O	4.0	0.7	0.6	25.3	-0-	-0-
z A	90.9	4.1	3.8	61.6	1.9	1.1
SIM D, °C						
1BP		69	90	-16	2	
10%		154	159	89	86	
20%		182	183	116	115	
50%		211	211	181	173	
90%		260	260	231	228	
FBP		339	327	276	271	



TABLE 50

## HYDROTREATER PRODUCT

RUN NO. R-139

SAN ARDO RERUN OF 139, M.B. 1

	JP-8	
	Feed	MB1
API	37.7	40.8
H, Wt%	12.82	13.45
S, ppm	20	37*
N, ppm	1	0
FIA: S	65.5	80.9
V O	0.8	0.5
o		
1 A	33.7	18.6
%		
SIM-D, °C		
IBP	78	38
10%	141	133
20	168	160
50	212	204
90	272	252
FBP	329	301

\* Probably should be ~1 ppm. Answer high, likely due to dissolved or oxidized H<sub>2</sub>S.

TABLE 51

US MILITARY SPECIFICATIONS FOR TURBINE FUELS.<sup>14</sup>

Issuing Agency: Specification: Revision Date: Grade Designation: Fuel Type:		USAF MIL-T-5624L-Amd. 1 16 June 1980 JP-4 Wide-Cut		USAF MIL-T-83133A-Amd. 1 4 April 1980 JP-5 Kerosene		USAF MIL-T-83133A-Amd. 1 4 April 1980 JP-8 Kerosene		Test Method ASTM PTMS 791	
COMPOSITION	Acidity, Total (mg KOH/g)	MAX.	0.015	0.015	0.015	D 3242			
	Aromatics (vol %)	MAX.	25.0	25.0	25.0	D 1319			
	Olefine (vol %)	MAX.	5.0	5.0	5.0	D 1319			
	Sulfur, Mercaptan (wt %) (1)	MAX.	0.001	0.001	0.001	D 1322			
	Sulfur, Total (wt %)	MAX.	0.4	0.4	0.3	D 1266/D 2867/ D 2622			
	Color, Saybolt	MAX.	Report	Report	Report	D 156			
VOLATILITY  (D 2867 Limits in parentheses)	Distillation								
	Temp. Init. BP (°C)	MAX.	Report	Report	Report	D 86/D 2867			
	Temp. 10% Rec (°C)	MAX.	Report	206 (185)	206 (186)				
	20% Rec (°C)	MAX.	145 (130)	Report	Report				
	50% Rec (°C)	MAX.	190 (185)	Report	Report				
	90% Rec (°C)	MAX.	245 (250)	Report	Report				
	Final BP (°C)	MAX.	270 (320)	290 (320)	300 (330)				
	Residue (vol %) (for D 86)	MAX.	1.5		1.5				
	Loss (vol %) (for D 86)	MAX.	1.5		1.5				
	Explosiveness, Percent	MAX.		50		1151 FED STD 791			
	Flash Point (°C)	MAX.		60	38	D 93 (2)			
	Gravity, °API (15°C)	MAX.	45-57	36-48	37-51	D 1296			
	Density, 15°C (kg/m³)	MAX.	781-802	788-845	775-840	D 1296			
Vapor Pressure (37.8°C), kPa (psi)		14-21 (2.0-3.0)	-		D 323/D 2551				
FLUIDITY	Freezing Point, °C (°F)	MAX.	-58 (-72)	-46 (-51)	-50 (-58)	D 2296			
	Viscosity @ -20°C (cSt)	MAX.	-	8.5	8.0	D 445			
COMBUSTION	Aniline-Gravity Product or Net Heat of Comb., MJ/kg (Btu/lb)	MIN.	5250	4500		D 1406			
		MIN.	42.8 (18,400)	42.6 (18,300)	42.8 (18,400)	D 2362/D 3338			
	Smoke Point	MIN.	20.0	19.0	19.0	D 240 (3)			
	or Hydrogen Content (wt %)	MIN.	13.6	13.5	13.5	D 1322 D 1018/D 3343/ D 3701 (4)			
CORROSION	Copper Strip (2 hrs @ 100°C)	MAX.	1b	1b	1b	D 130			
STABILITY	JFTOT ΔP (mm Hg)	MAX.	25	25	25	D 3241 (9)			
	JFTOT Tube Color Code	MAX.	< 3	< 3	< 3				
CONTAMINANTS	Existent Gum (mg/100 ml)	MAX.	7	7	7	D 381			
	Particulates (mg/liter)	MAX.	1	1	1	D 2276 (5)			
	Water Reaction Interface	MAX.	1b	1b	1b	D 1094			
	Water Separation Index Modified	MIN.	70 (6)	85 (8)	70 (6)	D 2580			
	Filtration Time (minutes)	MAX.	15	-		(5)			
ADDITIVES	Anti-Icing (vol %)		0.10-0.15	0.10-0.15	0.10-0.15	S330, S340,			
	Antioxidant		Required (7)	Required (7)	Option	3527 FED STD 791			
	Corrosion Inhibitor		Required	Required	Required				
	Metal Deactivator		Option	Option	Option				
	Antistatic		Required		Required				
OTHER	Conductivity (pS/m)		200-600		200-600	D 2624/D 3114			
	Service NATO Code No.		All F-40	Navy F-44	USAF F-34; F-35 (10)				

NOTES: (1) The mercaptan sulfur determination may be waived if fuel "Doctor Sweet."

(2) D 56 also applicable to JP-8.

(3) D 3338 only allowed for JP-4 and JP-8.

(4) D 3343 only allowed for JP-4 and JP-8.

(5) Minimum one-gallon sample. Filtration time in accordance with Appendix A of MIL-T-5624L also used for D 2276 particulate.

(6) With all additives except electrical conductivity additive.

(7) If hydrogen treated blend stocks used - Optional if no hydrotreating used.

(8) With all additives except the corrosion inhibitor additive or 70 with all additives present.

(9) Test at 280°C tube temperature.

(10) Same as JP-8 without additives.

hydrogen content. Aromatics must be  $\leq 25$  vol% for both JP-4 and JP-8; hydrogen content must be at least 13.6 wt% for JP-4 and 13.5 wt% for JP-8; JP-4 gravity must lie within 45 to 57°API, and JP-8 gravity must lie from 37 to 51°API (at 15°C). When aromatics, gravity, and hydrogen content are satisfied, most other specifications are easily met with proper product handling and distillation adjustment.

The Sunnyside precursors easily passed the aromatics, gravity, and hydrogen specification at mild hydrotreating conditions of 650°F, 800 psig, and two liquid hourly space velocity (Table 46).

The Hondo JP-8 required moderately severe conditions of 700°F, 1200 psig, 0.75 LHSV to achieve acceptable aromatics; the Hondo JP-4 feed had a relatively high hydrogen content and needed less severity to treat. The two Hondo feeds had high (2.5 to 3 wt%) sulfur, but that was also easily reduced to below specification levels at the conditions tested.

Both Westken JP-4 and JP-8 hydrotreater feeds had very low hydrogen content and high aromatic character, so both were treated severely. The JP-8 hydrotreater products each contained only about 4 vol% aromatics, and the JP-4 products were less than 2 vol% aromatics each, so the Westken was somewhat easier to treat than predicted, especially the JP-4.

The JP-8 gravities lie close to the specification limit, but the JP-4 gravities fell right into specification midrange. Since the hydrogen consumptions of the Westken fuels were so high (2200-3000 SCFB) and the aromatics contents were so low, less severe treating could probably still give on-spec products. Reducing process pressure would decrease both hydrogen consumption and utility costs.

The San Ardo products were more difficult to treat than predicted. The JP-4 met aromatics, gravity, and hydrogen by hydrotreating at 700°F, 1200 psig, and 0.75 LHSV. At the same conditions, the JP-8 did not meet hydrogen and aromatic content requirements. The JP-8 product from material balance 1 (Table 47) was retreated to yield an acceptable JP-8 in Run 139R (Table 50), at 700°F, 1000 psig, and 0.75 LHSV. Hydrogen content was still slightly below specification limit.

One general trend for all runs was that the JP-4's seemed to hydrotreat more easily than the JP-8's. This was not unexpected since the JP-4 precursors generally had lower aromatics and sulfur contents and higher gravities and hydrogen contents, and because lighter boiling components, in general, require less hydroprocessing severity.

High degrees of nitrogen and sulfur removal were exhibited in all the tests. Sunnyside samples showed >93% and San Ardo showed >99% removal of both sulfur and nitrogen. Hondo samples had >99% sulfur and >95% nitrogen removed; Westken samples had >98% sulfur and >99% nitrogen removed.

### Conclusions

- Successful JP-4 and JP-8 hydrotreated samples were made at the conditions tested, except for San Ardo JP-8. An acceptable San Ardo JP-8 was made by treating it a second time.
- Necessary treatment severity appeared to increase in the order Sunnyside (as received) < Hondo < San Ardo < Westken.
- Although the Hondo precursors had relatively high sulfur contents, they did not interfere in the hydrotreating process, and aromatics/gravity/hydrogen content modifications were easily obtained.
- The conditions used on the Westken were more severe than necessary, especially for the JP-4, as the aromatic contents of the products were much lower than required.

#### IV. TURBINE FUEL SAMPLES

A total of eight aviation turbine fuel samples were prepared from four varying feedstock sources in order to meet military specifications for JP-8 and JP-4 fuels. This section describes the final processing treatments used to upgrade each of the eight samples previously described to acceptable fuels. These efforts describe the extent and variety of processing treatments to which the tar sand and heavy oil-derived jet fuels must be subjected following the process variable response portion of the Phase II experimental work.

The feedstocks for this portion of work consisted of one hydrotreated JP-8 sample and one hydrotreated JP-4 sample from each of the four feeds. Each fuel sample was previously processed sequentially through metals removal, Reduced Crude Conversion<sup>SM</sup>, and hydrotreatment modules with product fractionation and analysis provided following each processing step.

Each of the eight product fuel samples were handled identically through several processing phases, and then were analyzed to determine what laboratory upgrading steps were necessary.

### Experimental Procedure

All of the fuel samples produced were stabilized or fractionated on a laboratory distillation column manufactured by Todd Scientific Co. The Todd column is a 35"x1" glass column packed with 4mm glass helices in random fashion, providing a separating efficiency equivalent to about 40 theoretical plates. The column is externally heated and is equipped with a mechanical vacuum pump capable of maintaining operation in the 0-20 mm/Hg pressure range routinely.

Each fuel sample, following hydrotreatment, was stripped on a Todd distillation column to eliminate dissolved gases and unwanted byproducts of hydroprocessing. Following this processing step, the histories of each of the fuel samples differ considerably and each will be summarized here briefly.

#### Westken JP-8

The hydrotreated sample was stripped on a Todd column until 40 mls. of overhead was collected. The hydrocarbon aliquot recovered was scrubbed with caustic pellets, washed three times with distilled water, filtered and recombined with the stabilized fuel sample.

Following analysis, the sample was distilled such that one-half of the material boiling above 450°F was removed in order to define an acceptable end point and to improve

freeze point. A high boiling base stock was used as a "chaser" in the distillation to facilitate complete carry-over of the fuel sample. Also, a 6 wt% fraction was removed from the front end to correct a low flash point. The sample was then bottled, nitrogen purged and sealed for shipment.

#### Westken JP-4

The hydrotreated sample was stripped by distilling and collecting a 100 ml aliquot, which subsequently was caustic scrubbed, water washed, filtered and recombined with the stabilized oil. Following analysis, the entire sample was distilled and collected over caustic pellets in order to meet copper corrosion specifications. A high boiling base stock was used as a "chaser" during the distillation. After final analysis, the shipment was bottled, nitrogen purged and sealed for shipment.

#### Hondo JP-8

This hydrotreated fuel sample was stripped as described in previous examples, followed by treatment over a bed of attapulgu clay to improve sample color. Next the sample was distilled completely and collected over caustic pellets to remove corrosive agents. A 10 wt% cut was removed from the front end to improve flash point, and about one-half of the liquid boiling above



about 400°F was removed to define the endpoint and to improve freeze point. A high boiling base stock was used in the distillation as a "chaser." Following analysis, the sample was bottled, nitrogen purged and sealed for shipment.

#### Hondo JP-4

The hydrotreated sample was stripped as described previously. Because of high corrosion values in the fuel, the sample was subjected to several treatments. Ultimately, successful response to copper corrosion analysis was attained only after distilling the total sample and collecting it over caustic pellets. As before, a high boiling base stock was used as a "chaser" in the fractionation. After analysis, the sample was bottled, nitrogen purged and sealed for shipment.

#### San Ardo JP-8

After stripping the hydrotreated sample, the stabilized product was again distilled in total to its endpoint and collected over caustic pellets. An 8 wt% cut was removed from the front end to improve the flash point. A high boiling base stock was used as a "chaser." After analysis, the sample was bottled, nitrogen purged and sealed for shipment.

#### San Ardo JP-4

After stripping the hydrotreated sample, the entire fuel sample was redistilled to its endpoint and collected over caustic pellets, using a high boiling base stock as a "chaser." After analysis, the sample was bottled, nitrogen purged and sealed for shipment.

#### Sunnyside JP-8

Following stripping, the hydrotreated product was treated over a bed of attapulgus clay to improve product color. The fuel was then distilled to 250°F to establish an acceptable initial boiling point, then one-half of the liquid boiling above 400°F was removed to improve freeze point. The total sample was condensed over caustic, using a high boiling base stock as a "chaser," and was then bottled, nitrogen purged and sealed for shipment.

#### Sunnyside JP-4

The hydrotreated fuel sample was stripped as before, followed by distillation to its endpoint using a high boiling base stock as a "chaser." One-half of the 400°F+ liquid was removed to improve freeze point, and all liquid distillate was collected over caustic pellets. The final sample was then analyzed, bottled, nitrogen purged and sealed for shipment.

### Discussion

The experimental work resulted in the production of eight high quality fuel samples, (Tables 52-53), and applicable military fuel specifications were met with only minor exceptions. Of the four feed source oils, the Westken and San Ardo fuel samples were highly naphthenic and represent modest increases in fuel density. Sufficient quantities of each fuel were produced to satisfy Air Force contract requirements.

The major processing problems encountered in upgrading the fuel samples resulted from the nature of in-house laboratory handling practices as opposed to any anticipated processing in a fully integrated refining facility. Excessive laboratory handling and exposure of samples to the atmosphere resulted in oxidation and weathering of samples. Some laboratory samples failed ASTM D130 "Copper Strip Corrosion" due to oxidized sulfur species which would normally not be present after refinery hydrotreatment. These corrosive species were removed only after distillation over caustic pellets. Oxidation during sample handling is also thought to be responsible for high gum levels present in the final fuel samples.

Heteroatom levels in the finished fuels were extremely low, as much as an order of magnitude lower in the case of sulfur than called for in the military JP-4 and JP-8 specifications.

TABLE 52

TURBINE FUEL SAMPLES

	MILITARY SPECIFICATION JP-4	WESTKEN JP-4	HONDO JP-4	SAN ARDO JP-4	SUNNYSIDE JP-4
TOTAL ACIDITY, MG KOH/G	0.015	0.004	0.005	0.001	0.002
AROMATICS, VOL%	25.0	2.2	12.4	13.5	14.2
OLEFINS, VOL%	5.0	0.7	0.3	0.3	0.5
TOTAL SULFUR, WT%	0.4	0.008	0.003	0.003	0.001
COLOR, SAYBOLT	REPORT	+30	+30	+27	+30
DISTILLATION: D2887					
IBP °F	REPORT	69	71	69	75
10	REPORT	170	163	167	147
20	266	215	208	215	197
50	365	308	300	327	287
90	482	411	436	440	419
EP	608	483	503	497	484
GRAVITY, °API	45-57	49.6	52.3	48.0	53.2
VAPOR PRESSURE, PSI	2 -3	2.5	1.5	0.8	1.2
FREEZE POINT, °F	-72	<-90	-85	<-90	-77.8
HYDROGEN CONTENT, WT%	13.6	14.1	14.1	14.0	14.0
COPPER STRIP CORROSION	1b	1b	1b	1b	1b
EXISTENT GUM, MG/100 ML	7	1.6	25	7.4	2.0

TABLE 53

## TURBINE FUEL SAMPLES

	MILITARY SPECIFICATION JP-8	WESTKEN JP-8	HONDO JP-8	SAN ARDO JP-8	SUNNYSIDE JP-8
TOTAL ACIDITY, MGKOH/G	0.015	0.003	0.002	0.003	0.013
AROMATICS, VOL%	25.0	4.2	22.0	18.9	20.6
OLEFINS, VOL%	5.0	1.0	0.5	1.0	0.5
TOTAL SULFUR, WT%	0.3	0.003	0.03	0.004	0.002
COLOR, SAYBOLT	REPORT	+30	+30	+30	+30
DISTILLATION: D2887					
IBP°F	REPORT	259	264	244	275
10 %	367	332	311	317	350
20 %	REPORT	364	340	350	385
50 %	REPORT	408	407	412	421
90 %	REPORT	475	481	493	461
EP	626	564	559	574	491
FLASH POINT, °F	100		117		144
GRAVITY, °API	37-51	38.0	43.3	41.2	44.7
FREEZE POINT, °F	-58	-68.8	-57.1	-69.7	-31
VISCOSITY @ -20°C, CST	8.0	5.05	4.44	4.19	4.83
HYDROGEN CONTENTS, WT%	13.5	13.6	13.6	13.5	13.8
COPPER STRIP CORROSION	1b	1b	1b	1b	1b
EXISTENT GUM, MG/100 ML	7	11.8	11.0	5.2	15.2

Hydrogen contents, a major indicator of fuel quality, were well above specification levels in all samples except the San Ardo JP-8.

Freeze point modification was accomplished through hydrotreatment followed by distillation for each fuel sample. Specification limits were met easily for six of the fuel samples. The Hondo JP-8 sample was  $<1^{\circ}\text{F}$  deviant from the specification level. The Sunnyside JP-8 fuel sample had a significantly higher freeze point than the target of  $-58^{\circ}\text{F}$ , probably due to paraffinic (possibly higher-sourced) materials, but further processing of the sample was not practical.

Existent gum levels were acceptable for three of the fuel samples, but reached off-specification levels for the other five fuels. This trait is easily attributable to sample processing histories and handling techniques and is in no way indicative of any overall process inadequacies.

Vapor pressure specifications were met for one of the four JP-4 samples. The low vapor pressure found for these JP-4 fuel samples is attributed to excessive sample handling, leading to weathering of light ends.

### Conclusions

- JP-4 and JP-8 fuel samples were successfully produced in specified quantities for each of the four feed source oils.
- The Westken and San Ardo fuel samples are highly naphthenic and represent modest increases in fuel density.
- Heteroatom levels in the finished fuels are extremely low.
- Hydrogen content is at or above specification levels for each of the fuel samples produced.
- Essentially all physical and chemical property specifications of major significance were met, with the exception of the Sunnyside JP-8 freeze point.

## SECTION V. ECONOMICS UPDATE

Preliminary economics were developed during Phase I based on LP modeling of projected feedstock response to the processing scheme selected. Phase II economics efforts focus on a simple update of the Phase I model based on Phase II laboratory data. Final efforts in Phase III will encompass an overall view based on updated economic and experimental factors for the entire program.

The Phase II update is based on the same economic parameters used for Phase I analysis; details of these parameters are available in the Phase I report. In general, capital costs were estimated by module costs from open literature sources, with offsites costed at 45% of onsite facilities. A time base of 1983 (CE Index = 319) was used. Plant sizes were fixed by a flow of 50,000 BPCD to the demetallization section, including diluent where required. A discounted cash flow rate of 15% for a 100% equity funded plant was used.

Operating costs and feedstock values were estimated to be comparable to mid-1983 levels. All prime plant products (gasoline, distillate, and turbine fuels) were valued equally, with their actual cost calculated based on a \$25/barrel feedstock expense. For interest, a feedstock value was also calculated based on an average prime product value of 84 cents per gallon.



### Hondo

Few changes were required for the Hondo model, with actual laboratory data used to replace predicted data elements. In general, the Hondo processing response was similar to that originally predicted. As expected, sulfur specifications were often the driving force for process flow selections.

The major difference between Phase I and Phase II results were the high native naphtha content of the Hondo stock. Limited literature data led to the assumption in Phase I of zero naphtha content; the actual measured 17% naphtha yield changes processing slightly while making the 430+°F feedstock significantly more refractory than expected.

Overall results for the Hondo oil are summarized in Table 54. Downstream process modules are smaller in Phase II, due to the actual naphtha content, resulting in a slightly lower capital cost. However, the more refractory bottoms also results in slightly lower total plant yields, particularly of distillate and LPG. These impacts result in a net cost increase of about \$1 per barrel for the Hondo products, primarily due to decreased byproduct revenues (LPG) and increased utility costs, primarily sorbent and catalyst required by the three-fold increase in metals content over that originally expected. In general, however, the earlier predicted values are reasonably verified by the Phase II data.

**TABLE 54**  
**SUMMARY ECONOMIC RESULTS COMPARISON**

	Westken		Hondo		San Ardo
	Phase I	Phase II	Phase I	Phase II	Phase II
<b>Investment Data, MM\$</b>					
Fixed Capital	360	436	509	491	486
Working Capital	25	19	40	36	36
<b>Material Flows, BPCD</b>					
<b>Inputs:</b>					
Bitumen	29999	25000	49948	50000	50000
Isobutane	4634	2094	7010	4240	5995
Normal Butane	2144	998	3152	2316	2546
<b>Products:</b>					
LPG	1240	191	1872	384	440
Gasoline	25979	19038	37364	37650	39187
JP-4	2524	2123	5248	4949	4586
Diesel Fuel	3461	3101	10323	7335	8889
Residual Fuel	630	-	-	-	-
<b>Product Cost \$/BBL at 15% DCF:</b>					
Startup	0.20	0.28	0.17	0.17	0.16
Working Capital	0.34	0.27	0.32	0.24	0.23
Byproducts	(1.46)	(0.37)	(1.23)	(0.66)	(0.34)
Fixed Costs	2.04	2.83	1.62	1.71	1.54
Income Taxes	3.22	5.15	2.74	2.79	2.61
Utilities	3.31	4.82	3.13	3.73	2.85
Capital	5.62	8.89	4.72	4.88	4.58
Raw Materials	<u>29.90</u>	<u>29.63</u>	<u>29.43</u>	<u>29.01</u>	<u>28.67</u>
Prime Product Cost, \$/BBL	<u>43.20</u>	<u>51.50</u>	<u>40.90</u>	<u>41.90</u>	<u>40.30</u>
Feedstock Value, at \$0.84/gallon prime product Value, \$/BBL	19.10 <sup>a</sup>	11.60	-	19.80	21.30

a - Phase I estimate only

To get a better perspective on today's marketplace, these same flows and costs were utilized to calculate a net feedstock value. Sales of gasoline and distillate were costed at 84 cents per gallon, and the value of the Hondo oil calculated assuming no other changes. On this basis, the Hondo was valued at about \$20 per barrel.

### San Ardo

San Ardo was not evaluated in Phase I, so all comparisons for the oil will be made with the Hondo stock. Since in general the San Ardo is heavier and more aromatic, poorer yields would be expected except for the significantly lower sulfur content in the San Ardo. The Hondo oil begins with a 5% sulfur penalty which is directly reflected in product yields. Calculated economic results verify this penalty.

San Ardo plant size and flows are very similar to the Hondo case, with slightly better plant yields. However, the use of steam reforming versus partial oxidation (due to the sulfur content of the Hondo resid) reduces fixed costs for the San Ardo, while the lower metals content contributes significantly to reduced utilities costs. Increased plant yields also decrease per barrel raw material costs, with the net result of product valued at \$40.30/barrel - \$1.60 less than the Hondo oil. This difference is also reflected in

the feed value calculation, where the San Ardo oil is valued at about \$21 per barrel. Note that these values and differentials are for a high conversion distillate fuels refinery; for other cases, particularly asphalt refineries, relative values could easily change.

#### Westken

The Westken oil is easily the most refractory of these feedstocks, with evaluation of the Phase II data somewhat difficult. Since dilution of the Westken was required for processing, a petroleum LCO was used. This diluent introduces a significant confounding factor in evaluating modules downstream of the demetallization step.

Major differences in the Phase II process responses compared to the Phase I analysis are:

- Lower bitumen throughput at constant plant size, since operation at 30-40% dilution was not demonstrated; 50% dilution was required.
- Lower gasoline yield, probably due to the carry-through of refractory (non-hydrotreated) LCO to the RCC unit; while hydrotreated diluent is used in the overall model, the RCC model data are based on raw stocks.
- Increased capital cost, due to higher diluent handling requirements and in particular a very large increase in distillate hydrotreater costs due to high use of hydrotreated diluent.

In general, the Phase II analysis probably over-penalizes the Westken material. More complete analyses are underway in Phase III to resolve these problems. In addition, economics of scale penalize the Westken relative to the other two oils. Increasing the plant size to 50,000 BPD of raw feed to each plant would be a more valid comparison of individual feedstocks.

As a result, we expect the Westken product costs derived from Phase III to be somewhere between the Phase I (\$43.20/barrel) and Phase II (\$51.50/barrel) estimates. Likewise, the value should be somewhere between \$12-19/barrel for the Westken feedstock used in a high conversion fuels refinery.

#### Sunnyside

Sunnyside was not evaluated due to high levels of uncertainty in the data caused by poor sample integrity.

#### REFERENCES

1. Bartick, H., et. al., "Final Report - The Production and Refining of Crude Shale Oil Into Military Fuels, " Contract No. N00014-75-C-0055 (August, 1975).
2. Gallagher, J. P., et. al., "Synthesis and Analysis of Jet Fuels from Shale Oil and Coal Syncrudes," Contract No. NAS3-19747 (November, 1976).
3. Taylor, W. F., et. al., "Evaluation of Methods to Produce Aviation Turbine Fuels from Synthetic Crude Oils - Phase III," Contract No. F33615-74-C-2036 (June, 1977).
4. Robinson, E. T., "Refining of Paraho Shale Oil into Military Specification Fuels," Contract No. N00014-77-C-0750 (February, 1979).
5. Moore, H. F., and R. P. Long, "Refining of Military Jet Fuels from Shale Oil," Part IV, Contract F33615-78-C-2080 (August, 1982).
6. Sikonia, J. G., et. al., "USAF Shale Oil to Fuels," Part II, Contract F33615-78-C-2079 (July, 1982).
7. Reif, H. E., et. al., "An Exploratory Research and Development Program....," Part V, Contract F33615-78-C-2024 (March, 1982).
8. Moore, H. F., C. A. Johnson, W. A. Sutton, L. M. Henton, and M. H. Chaffin, "Aviation Turbine Fuel From Tar Sands Bitumen and Heavy Oils, Part I - Process Analysis," Contract F33515-83-C-2301, AFWAL-TR-84-2070, Part I, (September, 1984).
9. Moore, H. F., "Jet Fuel Production From Tar Sands and Heavy Oil by Asphalt Residual Treatment/Reduced Crude Conversion Process," USAF Aviation Turbine Fuels, 1985 Technology Review, Dayton, Ohio (March 26-27, 1985).
10. Zandona, O. J., et. al., "Reduced Crude Conversion - An Inexpensive Route to High Octane Gasoline," 80th Annual NPRA Meetin, San Antonio (March 21-23, 1982).
11. Zandona, O. J., et. al., "Reduced Crude Processing with Ashland's RCC<sup>SM</sup> Process," 47th Midyear Refining Meeting, API, New York (May 13, 1982).
12. Barger, D. F., and C.B. Miller, "Residual Oil Conversion in Ashland FCC Units," NPRA Annual Meeting, (March 20-22, 1983).

13. Busch, L. E., et. al., "Reduced Crude Oil Conversion in Commercial RCC<sup>SM</sup> and ART<sup>SM</sup> Process Operations," 1984 NPRA Annual Meeting, San Antonio (March 25-27, 1984).
14. Anon, "Handbook of Aviation Fuel Properties," Coordinating Research Council, Inc., CRC Report No. 530, (1983).

## LIST OF SYMBOLS AND ABBREVIATIONS

ACS	American Chemical Society
AICHE	American Institute of Chemical Engineers
AOI R&D	Ashland Oil, Inc., Petroleum Research and Development Department
*API	American Petroleum Institute liquid gravity scale
ART <sup>SM</sup>	Asphalt Residual Treatment, a service mark of Engelhard Corporation for professional services relating to selective vaporization processes for removing contaminants from petroleum feedstocks.
ASTM	American Society for Testing and Materials
BBL	barrels, 42 US gallons
BPCD	barrels per calendar day
BPD	barrels per day
BuMine	Bureau of Mines, U.S. Government
CE	Chemical Engineering Magazine
concarbon	Conradson carbon
cps	centipoise
cst	centistokes
C <sub>3</sub>	propane
C <sub>4</sub>	butane
C <sub>5</sub>	pentane
C/O	catalyst-to-oil weight ratio
DCF	discounted cash flow
deg.	degrees
DF-2	diesel fuel



# LIST OF SYMBOLS AND ABBREVIATIONS (CONT'D)

DOD	United States Department of Defense
DOE	United States Department of Energy
ed	edition or editor
eff	efficiency
EPA	Environmental Protection Agency, U.S. Government
est.	estimated
FIA	fluorescent indicator adsorption
°F	degrees Fahrenheit
FCC	fluid catalytic cracker or cracking
FOE	fuel oil equivalent
ft.	feet
Grav.	gravity
HCO	heavy cycle oil
HDS	hydrodesulfurization
HF	hydrogen fluoride
Hg	mercury
H/C ratio	hydrogen to carbon weight ratio
HPLC	high performance liquid chromatography
Hr	hour
IC <sub>4</sub>	isobutane
I.D.	inside diameter
IGT	Institute of Gas Technology

# LIST OF SYMBOLS AND ABBREVIATIONS (CONT'D)

JP-4	MIL-T-5642 jet fuel
JP-8	MIL-T-83133 jet fuel
K factor	Watson K factor, defined as the cube root of the volumetric average boiling point, in °Rankine, divided by the specific gravity.
KwHr	Kilowatt-Hour
lbs.	pounds, avoirdupois
LCO	light cycle oil
LETC	Laramie Energy Technology Center (now Western Research Institute)
LHSV	liquid hourly space velocity
LP	linear programming
LPG	liquified petroleum gases
M	thousand
m	meter
mm	millimeter
m <sup>3</sup>	cubic meter
MAT	microactivity test
MAV	maleic anhydride value
md	millidarcies
ml	milliliter
MGT	management
NC <sub>4</sub>	normal butane
Ni	nickel
No.	number

LIST OF SYMBOLS AND ABBREVIATIONS (CONT'D)

NPRA	National Petroleum Refiners' Association
NTIS	National Technical Information Service (U.S. Government)
OP.	operation
ppm	part per million (by weight unless specified)
PREP.	preparations
psi	pounds per square inch pressure
P.V.	pore volume
RCC <sup>sm</sup>	Reduced Crude Conversion, a registered service mark of Ashland Oil, Inc., for technical assistance and consulting services in connection with processes for heavy oil cracking and related catalysts.
RONC	research octane number, clear
ROSE <sup>sm</sup>	Residual Oil Supercritical Extraction, licensed by Kerr-McGee, Inc.
RPT	report
RVP	Reid vapor pressure, psig
sq.	square
SCFB	standard cubic feet per barrel (42 gallons)
USAF	United States Air Force
V	vanadium
visc.	viscosity
vol	volume
WABP	weight average boillint point
WBS	work breakdown structure

LIST OF SYMBOLS AND ABBREVIATIONS (CONT'D)

WHSV	weight hourly space velocity
wt	weight
2nd	second
10 <sup>9</sup>	billion
10 <sup>6</sup>	million
<	less than
>	greater than
@	at
%	percent
°	degrees
( )	byproduct credits when used in economic value tables
"	inch
\$	US dollars

END

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DTIC